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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of Geokhimiya we have chosen the system used by Chemical Abstracts, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

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DETERMINATION OF ABSOLUTE AGE BY THE CARBON^{14} METHOD

(Part II)

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(ABSTRACT)

In the article are given results of determination of the absolute geological age according to C^{14} of samples supposedly of the period of the Waldai glaciation of Eastern Europe and of the Zyryansk glaciation of Eastern Siberia, being of a synchronous age. Coal samples from archaeological excavations of the Khoresm expedition and samples of a scorched tree connected with the volcanic action on the Kamchatka peninsula have also been dated. The determinations of C^{14} were carried out simultaneously on two settings by means of counting the activity of the two gases, ethane and carbonic acid. The counting settings were improved in comparison to the settings previously described, as a result of which the background was lowered considerably.

This paper is a brief account of some of the results of age determinations of geological and archaeological samples by the C^{14} method. The determinations were made simultaneously with two instruments by counting the activity of two gases, ethane and carbon dioxide. This made it possible to compare the advantages and disadvantages of using C_2H_6 and CO_2 in age measurements.

In our first report [1] we described only the technique of using C_2H_6. Carbon dioxide requires more careful purification from foreign admixtures (O_2 and others) but is used predominantly at present [2-6].

It should be noted that for the synthesis of ethane, it is necessary to have a supply of hydrogen absolutely free of radioactivity of any kind. It is time consuming to check each cylinder of hydrogen, and we found that the synthesis of C_2H_6 with hydrogen prepared chemically in the laboratory (Zn + HCl) insures us against errors due to radioactive impurities.

It should be mentioned also that in the process of liberation and purification of the gases the yield of intermediate compounds was sufficiently near the theoretical to exclude the possibility of fractionation of carbon isotopes. Before measurement the liberated gases were allowed to stand in glass flasks for one month to insure complete decay of any radio that might have been present.

The one liter counters were filled with C_2H_6 or CO_2 by means of a special gas apparatus with a vacuum system until a gas pressure of 2 atmospheres was reached. Before the counters were filled the gases were purified once again in the gas apparatus by freezing at temperatures of -195.8°C and -78.5°C, respectively.

The counter assembly used for the age measurements presented below is considerably improved as compared with that described earlier. The proportional counters are arranged horizontally in an iron shield and surrounded by mercury shields, the shielding Geiger counters of type GS-30 used before have been replaced by counters GS-60, and in order to prolong their life there is a provision for damping discharges. The aggregate count from the ring of fourteen GS-60 counters and the differential count were recorded on a paper ribbon by automatic recorders EPP-09.

A general view of the counter assembly is shown in Fig. 1, and of the interior of the steel shield in Fig. 2.

As a result of the improvements the background count was considerably reduced. In the case of ethane, the measurement of the background with the new instrument gave 14.5 counts per minute for the 0.98 liter counter and 14.3 c/min for the 0.94 liter counter. The net count for modern carbon was 18.5 c/min.

The background rate for CO_2 in the 0.94 liter counter was 8.9 c/min. The net count for modern carbon was 9.5 c/min. In view of the effect of the hydrogen bombs and industrial waste, the modern carbon standard was a tree (birch) cut in Kamchatka in 1908. The standard for ancient carbon was a sample of marble from the Urals.

The change in the background rate with 10 millibar change in atmospheric pressure amounted to about 2.5%. The counting interval was 24 hours, and each sample was counted at least twice. It should be added that in the second instrument the number of the anticoincidence counters GS-60 and GS-30 was increased to 20 in the hope that by improving the shielding of the proportional counter the background would be decreased. This, however, did not decrease the background. Measurements by coincidence and anticoincidence between the proportional and shielding counters lead to the conclusion that the background rates given above are due mainly to impurities in the material of the counters and to uncharged particles.

The background was reduced by 11% by placing over the ethane-filled counters blocks 9 cm thick of paraffin mixed with boric acid. Surrounding the counter with such blocks except at the ends reduced the background by about 20%. In the case of ethane the minimum sample count was equal to three times the statistical error of the count, while in the case of CO_2 the minimum sample count was four times the statistical error of the count. This was based on the following considerations: 1) the net count of ethane is almost twice as high as for CO_2, and 2) the reproducibility of results is much better with ethane than with CO_2.

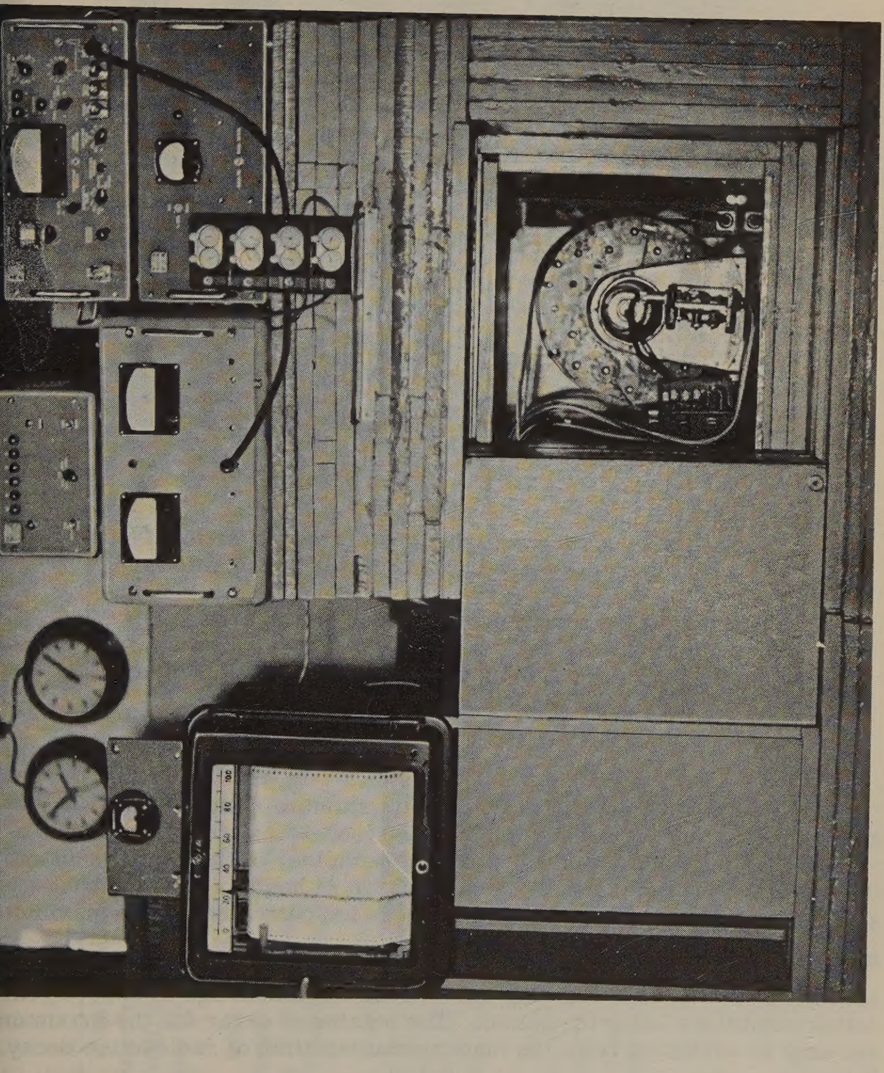

Fig. 1. General view of one of the assemblies for age determination by means of proportional counter

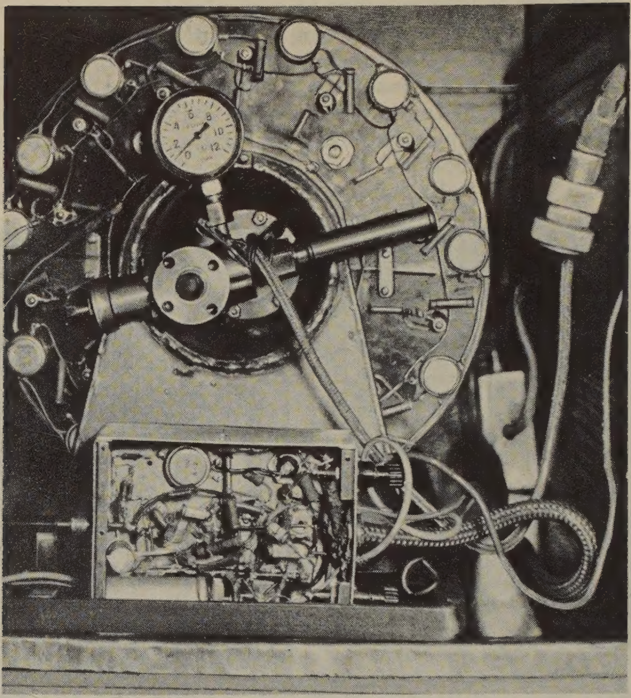

Fig. 2. The mercury shield with the proportional counter and Geiger counters in working position

In front of the proportional counter is a special valve with a "finger" and manometer. Below -- an arrangement for damping the discharges in the Geiger counters

Most investigators consider 3σ as the minimum sample count. To guarantee good measurements of CO_2, we took 4σ as the minimum.

Each measurement of ethane from the samples, of the background and of the modern carbon was usually continued for 24 hours. With the background rate, counting interval and $\underline{N}_{min}$ as indicated above, the maximum measurable age is 30,000 years (ethane $\underline{V}$ = 2 liters and $\underline{t}_{count}$ = 24 hours). For a 48 hour counting interval the maximum age is 33,000 years (other conditions being the same). The maximum error for the maximum age may be evaluated from the fundamental equation of radioactive decay. It is:

$$\Delta t = \frac{1}{3\lambda} \approx 2700 \text{ years (where } \lambda = \ln 2/\underline{T}_{1/2}\text{)},$$

if the count is three times the statistical error.

Sample No.	Description of material	Age in years	Gas	Instrument No.
M-34	Wood, Belorussian SSR, village of Gozha, right bank of the Nieman River, Outcrop No. 76, 1956 collection of Western Geological Administration. According to geological data the samepe is 18-20 thousand years old or more than 100 thousand years. Submitted by L. N. Voznyachuk, No. B-9.	8500 ± 300	CO_2	1
M-46	Peat and wood, Lithuanian SSR, Klaipeda region, village of Purmalei. Sample taken from a bed 0.4-0.6 m. thick at depth of 15 cm. Submitted by V. K. Gudelis, No. 2 (Inst. of Geology and Geography Acad. Sci. Lithuanian SSR)	6100 ± 230 6000 ± 240	C_2H_6 CO_2	1 2
M-6	Wood, Yaroslavl' district, from an outcrop on the right bank of the Dolgopolka River, 3 km east northeast of Tugaevo. Supposedly from lacustrine-paludal intermoraine deposit of the middle of the last interglacial stage. Submitted by the Department of Geology, Yaroslavl' Pedagogical Institute	$\geqslant 30,000$	C_2H_6	1
M-136	Wood. Yakutiya, left bank of the Vilyui River 1 km below the mouth of the Byrykan River. Sample taken from the depth of 1 m from the surface from the high floodplain deposits formed in part during the thermal optimum in the Holocene. Outcrop No. 4. A. V. Trofimov's collection of 1955. Submitted by M. N. Alekseev, No. 422. Supposed age 2-10 thousand years	Modern	C_2H_6	1
M-137	Wood, sample No. 423 from the same outcrop but from 2.5 m below surface. Supposed age 2-10 thousand years	1920 ± 120	C_2H_6	1
M-138	Wood. Yakutiya, left bank of the Vilyui River 5 km above Lankholokh landing. Outcrop No. 10, Collection of 1955. Supposed age 12-30 thousand years. Submitted by M.N. Alekseev, No. 441	$\geqslant 30,000$	C_2H_6	1

Table (Continued)

Sample No.	Description of material	Age in years	Gas	Instrument No.
M-139	Wood. Yakutiya, left bank of the Vilyui River, 4 km southwest of the mouth of the Tangnara River Outcrop No. 3. 1955 coll. Supposed age 12-30 thousand years. Submitted by M. N. Alekseev, No. 420	⩾30,000	C_2H_6	1
M-140	Wood fragment and peat from silt. Yakutiya, left bank of the Vilyui River, 5 km north of the mouth of the Tangnara River. Supposed age about the end of Q_3, 1953 collection. The character of the sediment points to increasing continentality of climate. Submitted by M. N. Alekseev, No. 125	⩾30,000	C_2H_6	1
M-141	Peat from lacustrine silt contorted by frost action. Yakutiya, left bank of the Vilyui River. Sample taken 10 m below surface, 14 km below the mouth of the Chebyda River. Supposed age - end of Upper Pleistocene, approximately the Sartansk (last) glacial stage. 1953 collection. Submitted by M. N. Alekseev, No. 219	⩾30,000 ⩾24,500	C_2H_6 CO_2	1 1
M-4	Wood. Igarka region. From a depth of 6.5 m, in the permanently frozen ground. Submitted by A. M. Pchelintsev (Obruchev Permafrost Institute, Acad. Sci. SSSR). Supposed age 3-5 thousand years	⩾24,500 ⩾24,500	CO_2 CO_2	1 2
M-91	Coal. Excavations of the Khorezm Expedition (Kara-Kalpak ASSR), Kanga-Kala, central building, room No. 1. Collected in 1955. Submitted by S. P. Tolstov. Supposed age IV c. A. D.	1780+180 1850±180	CO_2 CO_2	1 2
M-96	Coal. Excavations of the Khorezm Expedition. Koi-Kryglan-Kala, eastern sector, room No. 13-B, trench No. 7, collected in 1955. Submitted by S. P. Tolstov. Supposed age IV-II c. B. C.	2100±180	CO_2	1

Table (Continued)

Sample	Description of material	Age in years	Gas	Instrument No.
M-100	Coal. Excavations of the Khorezm Expedition. Kallaly-Gyr, tower 15, near the entrance to the large (lower) pottery kiln. Collected in 1953. Submitted by S. P. Tolstov. Supposed age II - III c. A. D.	1900±190 1780±180	CO_2 CO_2	1 2
M-129	Part of a charred log from a pumice bed deposited by an ancient eruption of Shiveluch. Beneath the moraine of the last glaciation. Kamchatka. Collected in 1955. Submitted by G. S. Gorshkov, No. 738. Supposed age 10-12 thousand years	1500±170	CO_2	1
M-130	Coal from a campsite of ancient Kamchadals. From the depth of 2. 7 m. The deposit is overlain by several beds of ash and lapilli from the gigantic eruptions of Shiveluch. Collected in 1955. Submitted by G. S. Gorshkov, No. 744. Supposed age about one thousand years	3100±200	CO_2	1

The samples reduced to CO_2 were also counted at the gas pressure of 2 atmospheres. In this case, under the same conditions, the time is shorter because the $\frac{N_{\text{Sample}}}{N_{\text{Background}}}$ ratio is less. However, for samples Nos. 91, 96, 100 and others, this was not important, for their ages fall sufficiently closely into the 24,500 year scale with the count interval of 24 hours and into the 27,000 year scale with the count interval of 48 hours.

This is the reason why the table shows different upper age limits for the same sample measured on ethane and on CO_2.

The liberation of gases, their purification and the construction of the counters, their filling and the counting procedure will be described in detail in another paper.

Below we present some absolute ages of geological and archaeological samples, among them some samples of wood from the deposits of the Valdai glacial stage of the European part of the USSR and the synchronous Zyryansk glacial stage of Eastern Siberia (Yakutiya).

Samples Nos. 138, 139, 140 and 141 were taken from outcrops along the Vilyui River (see Table and Fig. 3). As will be seen later, all of them are older than was supposed by geologists. Two samples, Nos. 136 and 137, near in age to modern carbon, were taken from the floodplain of the river [7].

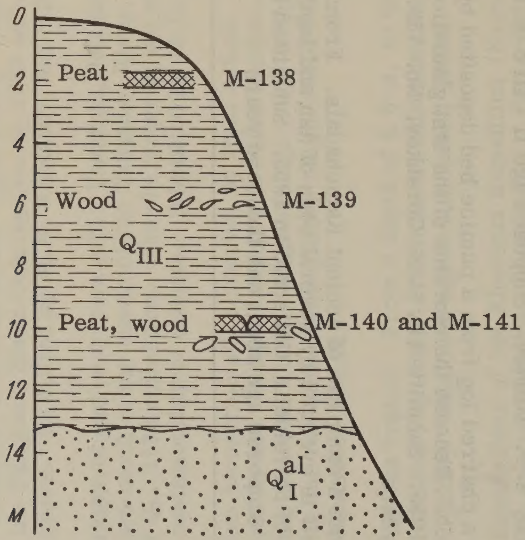

Fig. 3. Distribution of the samples taken from the surface deposits of silt and fine sand on the left bank of the Vilyui River [7]

Then there are samples, mainly coal, from the excavations of the Khorezm Expedition. These samples have been rather closely dated archaeologically, and it was interesting to determine their C^{14} ages. The radiocarbon ages of the Khorezm samples practically coincide with the archaeological dates based on the finds of coins and pottery [8].

Finally, we had a few samples of charred wood connected with an undated eruption of the volcano Shiveluch on Kamchatka Peninsula.

The Table gives a description of the samples, their supposed age and our data.

In the future we expect to use the two instruments available to us for direct age determinations of samples of interest to geologists and archaeologists.

We express our thanks to M. N. Alekseev, L. N. Voznyachuk, G. S. Gorshkov, V. K. Gudelis, A. M. Pchelintsev and S. P. Tolstov and others for providing us with geological and archaeological samples.

REFERENCES

1. Vinogradov, A. P., A. L. Devirts, E. I. Dobkina, N. G. Markova, and L. G. Martishchenko, Geokhimiya, No. 8, 3 (1956).
2. De Vries, Hl., G. W. Barendsen, and H. T. Waterbolk, Science 127, 129 (1958).
3. Fergusson, D. J., and T. A. Rafter, N. Z. J. Sci. and Technol. B-38, No. 7, 732 (1957).
4. Ostlund, H. G., Science 126, 493 (1957).
5. Broecker, W. S., and J. L. Kulp., Science 126, 1324 (1957).
6. Münich, K. O., Science 126, 194 (1957).
7. Alekseev, M. N., Byul. Komis. po izuch. chetvertichn. perioda AN SSSR, No. 21, p. 87 (1957).
8. Tr. Khorezmskoi Arkheologo-Etnograficheskoi Ekspeditsii, Vol. II (Report of the Khorezmian Archaeological-Ethnographic Expedition, Vol. II). Izd. Akad. Nauk SSSR (1958).

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METHOD FOR DETERMINING OXYGEN-ISOTOPE RATIOS IN ROCKS AND MINERALS

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(ABSTRACT)

In the article a method devised by the author is described for the reduction of rocks and minerals by graphite for the purpose of isotopic analysis of their oxygen. A description of the apparatus and of the procedure of carrying out the reaction is given. Experimental data of the reaction kinetics of the reduction of various rocks and on the completeness of the CO output are cited. The rock and mineral reduction by graphite is completed within 15—18 minutes in the temperature interval from 1000° to 1900°. The CO output for various materials ranges from 95 to 100% depending on their chemical composition. Procedures are described to achieve a high purity of the gas. The analysis of the obtained carbon monoxide shows that nitrogen and hydrocarbon impurities, which interfere with the isotopic CO analysis in the mass-spectrometer, are practically absent. The sources of error are analysed, and the reproducibility and the accuracy of the method is shown. The average error of the average value to be determined does not exceed 0.02% of relative values. The applicability of the method for various materials of investigation is shown, in particular for alumosilicate rocks containing alkalic and alkaline earth metals.

At the present time a considerable amount of data has been accumulated on the determination of oxygen isotope ratios in rocks, minerals and meteorites. It has been possible on the basis of these data to characterize some of the geochemical processes which go on in the earth's crust and which have determined the observed distribution of isotopes in nature. Further refinement of these data and their application to the study of rock and mineral genesis depends upon improvement in the methods of separating oxygen from samples and in techniques of isotopic analysis.

It has been shown experimentally that the maximum deviation of O^{18} in natural materials from the absolute O^{18} content in river water (0.2% abs. taken as 100%) is not more than 5%. It has also been shown (1) that within the limits of a particular class of compound e.g. one type of rock, the O^{18}/O^{16} ratio fluctuates from 0.50 to 0.06% (relative). Thus, the minimum value determined is 0.06% and less.

A fundamental experimental error can result from the incomplete liberation of oxygen from the mineral or rock. This may lead to difficulty in estimating the fractionation of its isotopes. Other errors may result from side reactions which occur during the process of oxygen liberation and which can lead to uncontrollable fractionation of oxygen isotopes. For example, the liberated gas containing the oxygen to be investigated, may become partially fixed by some extraneous agent or it may enter into isotopic exchange reactions with oxygen-bearing compounds. Moreover, in measuring oxygen isotope ratios in the mass-spectrometer the experimental error may be increased by contamination of the gas under study by oxygen from other sources or by gases having a mass equal to the mass of the gas being analyzed.

A number of early attempts [2, 3] to determine the isotopic composition of the oxygen of alumosilicates ended in failure, due primarily to the absence of a well-developed method for liberating oxygen. The accuracy of those experiments was ±1.5—±2.5%. Later on, a number of authors conducted extensive work on a method which has resulted in greater experimental accuracy. The existing data on the isotopic composition of oxygen in rocks have been obtained by the following methods: In 1947 [4] Vinogradov and Dontsova, first proposed a method for reducing rocks by means of spectrographically pure carbon at 2000°, which produced a yield of oxygen of 95-100%. The carbon monoxide obtained as a result of the reaction was reduced by hydrogen to methane and water, in a catalyzer. Isotopic analysis of the oxygen was carried out by density measurement. Experimental accuracy was + 0.15%. In the works of Baertschi [5] and Baertschi and Silverman [6] published in 1950-1951, a method was employed consisting of fluorinating a rock, and a combination of fluorination and chlorination at 430° in a platinum catalyzer. The oxygen yield was 80-100%. The isotopic analysis was done with the mass spectrometer. Experimental accuracy was ±0.15% to 0.05%. In 1952 Schwander [7] also employed the method of reducing a rock with carbon at 2000-2100°, after modernizing the apparatus. The carbon monoxide yield in this work amounted to 80%. The isotopic analysis of O^{18}/O^{16} was made from CO in the mass-spectrometer. Experimental accuracy was ±0.04%. In 1958 a method of reducing rocks with spectrally pure graphite at high temperatures was again employed by Vinogradov, Dontsova and Chupakhin [1] for obtaining data on the isotopic composition of oxygen in igneous rocks and meteorites. The yield of CO amounted to 95-100%. Experimental accuracy was plus or minus 0.02-0.04%. When the present paper was ready for the press, a paper by Clayton and Epstein [8] appeared. In their work the method of reducing minerals by carbon was used to determine the isotopic composition of the oxygen in natural oxides of silicon and iron. The carbon monoxide formed was recombined to CO_2, using a catalyst, and analyzed in the mass-spectrometer. The yield of carbon monoxide for the materials indicated was 100%. The precision of the determinations was ± 0.01 - 0.02%. The authors were unable to apply the graphite method of reduction to alumino-silicate rocks.

This article describes a method of reducing rocks and minerals with graphite at high temperatures for isotopic analysis of their oxygen. The authors discuss the kinetics of the reduction reaction of various rocks, the completeness of CO output, measures taken for attaining high purity of the gas, sources of error, reproducibility and accuracy of the method, and its applicability to the various materials under investigation.

The principle of the method involves the reduction of rocks by spectrographically pure graphite at temperatures up to 2000° in a vacuum furnace according to the reaction:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

Other oxides in the rock are reduced by analogous reactions. The carbon monoxide obtained is subjected to an oxygen isotope analysis in the mass-spectrometer according to the method described in [9].

Apparatus

The arrangement for reducing rocks is illustrated in Fig. 1. Here 1 is the vacuum furnace; 2 is the Langmuir mercury-vapor pump, which together with the fore-vacuum pump and a perfectly tight apparatus provides a vacuum of 10^{-5} mm Hg; 3 and 4 are the indicators of the thermocouple and ionization manometers, respectively; 5 is a Toepler-type pump, by means of which the carbon monoxide derived in the furnace as a result of the reduction reaction may be forced into the calibrated McLeod gage 6 and a part of it into ampules 7. After the ampules are unwelded from the

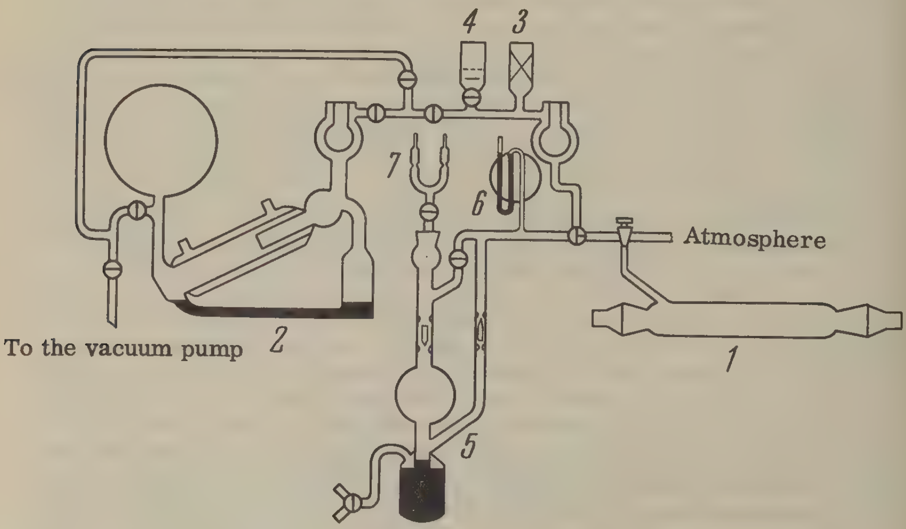

Fig. 1. Schematic drawing of the vacuum apparatus for reducing minerals and rocks with graphite. Explanations in the text

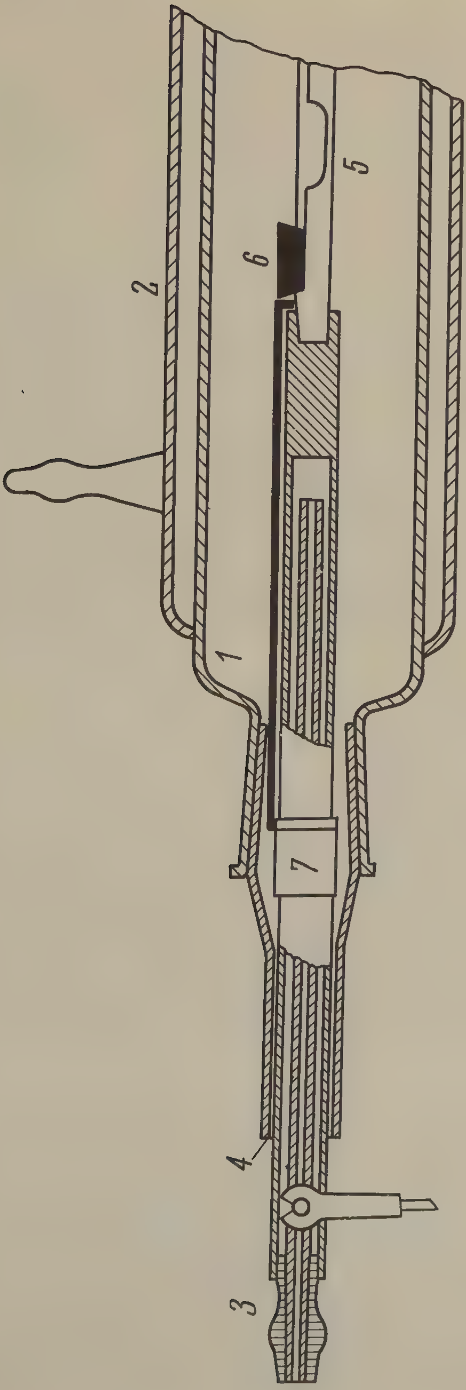

Fig. 2. Vacuum furnace for reducing minerals and rocks with graphite. Explanations in the text

instrument, the gas is transferred to the mass-spectrometer for isotopic analysis. The principle of construction for this vacuum furnace, was borrowed from the work of Schwander [7], and is as follows:

A graphitic resistance is firmly inserted between two leads in an evacuated cylindrical quartz vessel. In the middle part of the graphite rod a high temperature is developed over a small inteeval as a result of a sharp change in its cross section. The reduction reaction takes place at this part of the graphite rod.

The furnace is shown schematically in Fig. 2. It consists of a quartz cylinder, 1, with fitting ground joint surfaces on each end. An outer quartz cylinder, 2, is fused to it, and serves as a jacket for cooling by running water. Two cylindrical copper leads, 3, which are introduced from both ends through the ground joints, are also cooled by running water. The leads are set in rubber gaskets, 4, which serve also to seal the vacuum. The furnace is fed by current from a transformer having a primary potential of 200 volts, a secondary operating potential of about 8 volts and a power of about 5 kilowatts. Inside the furnace between the leads, is firmly fixed a graphite rod, 5, (with a conical fitting surface) about 10 cm long and about 1 cm think. This rod serves as a resistance. It is prepared of spectrographically pure graphite containing less than 0.06% of impurities. A depression is ground out of the middle of the rod in the form of a saddle about 2 cm long and as deep as possible. In it a combustion boat containing a charge is placed. The best possible contact is made between the graphite rod and the copper leads, so that the maximum resistance is concentrated in the depression in the middle of the rod, where, maximum heating is developed upon application of the current. The success of the experiment depends upon how localized the point of heating can be made. The temperature at the point of heating on the graphite rod is regulated by changing the primary potential of the transformer by means of a variac. Measuring the temperature at the point of heating is done by an optical pyrometer, accurate to within plus or minus 30°.

The combustion boat for the charge, 6, (0.75 g in weight, about 15 to 18 mm in length, 5 to 6 mm in width and about 8 mm high,) is prepared from the same graphite and has a tightly fitting lid with apertures for the escape of gas. An iron device, 7, in the form of a paddle attached to a ring may be moved along the left lead by means of a cylindrical electromagnet. In this manner the boat containing the material may be introduced into the depression on the graphite rod when the furnace is closed and evacuated. Following this operation, the iron paddle with the ring is removed by the electromagnet from the zone of heating to its original position.

Preparation for Conducting the Reduction Reaction

For an analysis a weighed sample of 50 mg is prepared. This assures a quantity of gas (from 30 to 40 cm^3 of CO, depending on the material for analysis), sufficient enough to minimize the effect of adsorption and isotopic exchange with substances contaminating the surfaces of the apparatus and possibly appearing on them in the course of the analysis. A sample of rock, finely ground in an agate mortar, is mixed well with a two or threefold, stoichiometric excess of spectrally pure graphite and placed in the cup. The cup is placed on the left end of the graphite rod and the furnace is closed. After exhausting the apparatus the graphite rod is degassed in the vacuum under pumping with a gradual rise in temperature at the point of heating from 900 to 2100°. On the average, degassing of the graphite rod is completed in 3 or 4 hours, fluctuating between 2-1/2 hours and 5-1/2 hours, depending on the state of the point of heating. When the degassing is finished a vacuum of $2\text{-}3 \cdot 10^{-5}$ mm Hg is attained.

In order to degas the inner surfaces of the furnace and to free them of residues of adsorbed organic solvents, with which the furnace is washed after each experiment, they are subjected, while the graphite rod is being degassed, to prolonged heating at 70-80° by passing hot water through the cooling jacket.

The boat with the charge is, in the main, degassed, since it is on the left end of the graphite rod by the lead, where a temperature of 800-900° is developed, while the maximum temperature at the point of heating is 2000-2100°. Final degassing of the boat is effected after complete degassing of the graphite rod, by moving it to the point of heating where the temperature is gradually increased from 900° to 1100-1400°, depending on the chemical composition of the sample. The temperature at which the combustion boat is degassed is increased until the beginning of the reduction reaction is indicated on the thermocouple manometer. It may be assumed that during degassing the sample loses, besides adsorbed and occluded gases, chemically bonded water. At the same time any carbonates are dissociated if these are present in small quantities in the sample. When the cup and charge have been degassed, the furnace is turned off and the apparatus is exhausted to a vacuum of $2\text{-}3 \cdot 10^{-5}$ mm Hg.

Reduction reaction

Upon reaching a vacuum of $2 - 3 \cdot 10^{-5}$ mm Hg, the reduction reaction is effectuated. The course of the reaction is evident from the formation of CO detected by the manometer. The reaction is judged to be complete when CO is no longer liberated. The reaction lasts 15-18 minutes. The reaction is conducted within the temperature interval from 1000 to 2000°. Special degassing and reaction procedures are set up for analyzing different materials, depending on their chemical composition.

Figs. 3 and 4 show how the amount of CO produced during the reduction of certain rocks and meteorites depends on the temperature of the reaction. Exposure at each temperature was 2 min. Toward the end of this time liberation of CO at the given temperature practically stopped, and the temperature was raised to the next level. An examination of the experimental data obtained makes possible the following conclusions:

1. Reduction of these samples of graphite under the conditions of the experiment begins at various temperatures. For quartz and granite the reduction reaction becomes noticeable at 1300-1400°; for dunite and olivine, at 1200°; and for basalt, diabase, and stony meteorites, at the interval 1000-1100°. The temperature at which the reduction reaction begins is related to the chemical composition of the material, which, therefore, determines the conditions under which the experiment is conducted. Table 1 gives the results of the analysis of the meteorite and rock samples. The kinetic curves of their reduction reactions are presented in Figs. 3 and 4.
2. For all practical purposes the reduction of all materials studied ceased at 1900°.
3. The yield of CO for different materials fluctuates between 95.0 and

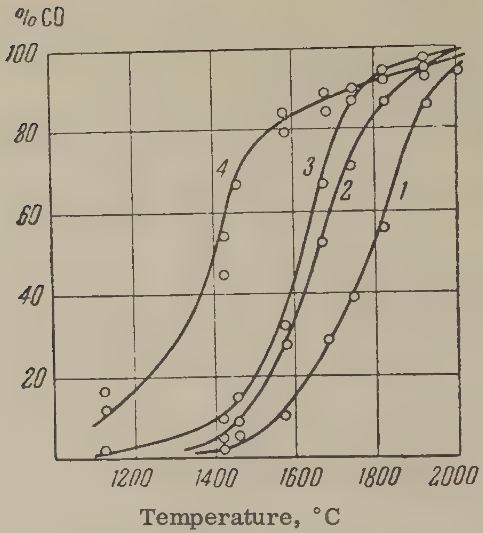

Fig. 3. Kinetic curves for the reduction of rocks by graphite. 1-dunite; 2-quartz; 3-granite; 4-basalt and diabase

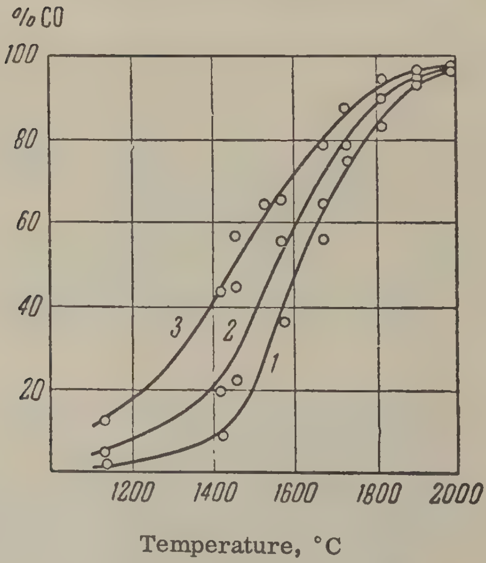

Fig. 4. Kinetic curves for the reduction of meteorites by graphite. 1-olivine from the iron-stony meteorite "Pallasovo zhelezo"; 2-chondrite "Saratov"; 3-achondrite "Vavilovka"

Table 1

Chemical composition of samples

	Meteorite "Pallasovo zhelezo" (olivine fraction)	Meteorite "Saratov" (chondrite)	Meteorite "Vavilovka" (achondrite)	Dunite, Polyarnyi Ural Syum-Keu, sample No. 1002	Basalt, Kamchatka, Klguchevskaya Volcano, erupted 1938	Diabase (taxitic), Noril'sk, sample No. 1036	Granite (trachytoidal), Ukraine, Novoukrainka
SiO_2	40.86	44.83	44.61	40.80	53.22	39.60	73.30
MgO	47.35	27.43	28.27	49.61	5.42	15.41	0.26
CaO		2.33	2.01	trace	8.60	7.94	0.46
Al_2O_3		1.80	1.82	0.97	17.28	12.14	12.33
FeO	11.72	14.46	20.18	6.35	6.22	9.05	1.28
Fe_2O_3				0.07	3.64	5.88	2.58
Na_2O		0.56	1.80	-	1.20	0.58	4.55
K_2O		0.10	0.29		0.11	0.35	4.20
TiO_2		0.12	-		0.80	0.74	0.11
Cl		0.01			0.02		
P_2O_5		0.74	-		0.10	0.05	0.05
MnO	0.43	0.39	0.86	0.14	0.20	0.20	0.02
S						2.00	
Cr_2O_3		0.71	0.17	0.28		0.22	
NiO							
FeS		6.53					
H_2O^+				1.11	0.08	$\left.\right\}$ 0.36	$\left.\right\}$ 0.86
H_2O^-				0.15	0.20		
V_2O_5						0.04	
BaO					2.90		
SO_3					0.06		
Residue						4.66	
Total	100.36	100.01	100.01	99.48	100.05	99.22	100.00

100%. The figures in table 2 show the CO yield during the reduction of the above-mentioned samples.

Table 2

CO Yield in the Reduction of Minerals and Rocks by Graphite

No. of exp.	Material analyzed	Weighed sample, g	Theoretical CO yield, cm^3	Actual yield, cm^3	Yield %
139	Quartz, Northern Urals, Neroika	0.0636	49.3	48.5	98.3
37	Olivine from meteorite "Pallasovo zhelezo"	0.0532	32.1	30.6	95.5
43	Meteorite (stony) "Saratov"	0.0500	29.9	28.7	96.0
118	Meteorite (stony) "Vavilovka"	0.0550	31.8	30.6	96.3
46	Dunite, Polyarnyi Ural, Syum-Keu	0.0500	30.3	28.8	95.0
85	Basalt, Kamchatka, Klguchevskaya volcano	0.0552	33.9	33.9	100.0
127	Diabase (taxitic), Noril'sk	0.0558	31.0	31.0	100.0
76	Granite (trachytoidal) Ukraine	0.0552	37.1	37.1	100.0

Table 3 contains results of the quantitative analyses of the carbon monoxide obtained. Analysis was performed by the semimicroanalytical method of fractional combustion and freezing out perfected by K. N. Florenskii. (Note: The author takes this opportunity to express her profound thanks to K. P. Florenskii and L. D. Kuznetskova for performing the analyses.) Accuracy of the experiment was plus or minus 0.05%.

Reproducibility of the Isotopic Analysis and Accuracy of the Experiment

The sufficiently complete yield of carbon monoxide, together with the analytical data on the composition of the gas, give a definite guarantee that there is no fractionation of oxygen isotopes due to incomplete liberation from the specimen under the conditions of the experiment. Analytical data show also that there are practically no admixtures of nitrogen or hydrocarbons in the gas analyzed, which might interfere with the isotopic analysis of CO in the mass-spectrometer.

Table 3

Composition of the gas Obtained From the Reduction of Meteorites and Rocks by Graphite

No. of exp.	Material analyzed	Content in %		
		CO	CO_2^*	N_2^{**}
138	Quartz	98.53	0.87	0.60
139	Quartz	99.50	none	0.50
37	Olivine from meteorite "Pallasovo zhelezo"	93.0	~2.0	<0.05
43	Meteorite "Saratov"	99.20	0.80	<0.05
118	Meteorite "Vavilovka"	100.00	none	<0.05
46	Dunite, Polgarnyi Ural	100.00	none	<0.05
85	Basalt, Kamchatka, erupted 1938	98.0	2.0	<0.05
127	Diabase, Noril'sk	99.55	none	0.45

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*H_2O and hydrocarbons except methane are determined along with CO_2.
**Inert gases and methane are determined along with N_2.

Table 4 shows the reproducibility of the isotopic analyses of carbon monoxide derived from the samples under study. The average error in the average determined value in these experiments does not exceed 0.02% relatively. In special rare cases it reached plus or minus 0.04%.

The mass-spectrometric technique for recording oxygen isotope ratios is described in [9] and we will not touch upon it in the present article. Mass-spectrometric data concerning isotopic analysis of oxygen are considered in terms of the difference between the O^{18}/O^{16} ratios in a sample and a standard, although in reality the ratio is $O^{18}/O^{16} + O^{17}$. In analyzing natural materials it is possible to disregard the enrichment of isotope O^{17} n view of its rarity. Where there is a maximum of 5% enrichment of both sotopes, O^{18} and O^{17}, the difference between the ratios O^{18}/O^{16} and $O^{18}/O^{16} + O^{17}$ will amount to about 0.003% relatively, assuming for the calculation normal O^{18}/O^{16} and O^{17}/O^{16} ratios equal to 0.002 and 0.0004, respectively. The error thus calculated on account of neglecting the enrichment of O^{17} is maximal and in practice will not reach this value, since, in conformance with the mass and distribution of O^{17}, a 5% enrichment of O^{18}, s accompanied by an enrichment of O^{17} not in excess of 2.5%. Moreover, he enrichment of O^{18} by 5% relatively, taken for the calculation, is a maximum. But even this calculated maximum error lies beyond the limits of ensitivity of the method of isotopic oxygen analysis used.

Isotopic Standard

The oxygen of large rivers (or of the ocean), which hold a relatively

Table 4

Reproducibility of Isotopic Analyses of Carbon Monoxide Derived from the Reduction of different rocks and meteorites

No. of exp.	Material	Source of Sample	Deviation from standard %	Average deviation from standard %	Average error of average value %
37	Olivine from meteorite "Pallosovo zhelezo"	Krasnoyarsk region RSFSR	-0. 74	-0. 74	$\pm$0. 0
38			-0. 74		
42	Meteorite (stony) "Saratov"	Saratov Province, RSFSR	-0. 75	-0. 73_5	$\pm$0. 015
43			-0. 72		
118	Meteorite (stony) "Vavilovka"	Kheronsk Province, USSR	-0. 67	-0. 66_5	$\pm$0. 005
122			-0. 66		
58	Dunite	Polyarnyi Ural, Syum-Keu Massif	-0. 78	-0. 76_6	$\pm$0. 007
59	"		-0. 76		
61	"		-0. 76		
85	Basalt	Kamchatka, Klyurevskaya volcano, erupted 1938	-0. 38	-0. 37_5	$\pm$0. 005
86	"		-0. 37		
125	Diabase (taxitic)	Noril'sk	-0. 41	-0. 41_5	$\pm$0. 005
127	"		-0. 42		
73	Granite (trachytoidal)	Ukraine, Novoukrainka	-0. 04	-0. 04_5	$\pm$0. 005
76			-0. 05		

constant O^{18}/O^{16} ratio, has been taken in a number of investigations as the isotopic standard of oxygen. This standard was used in most of the early work where the densimetric method of oxygen isotope analysis was employed.

In changing to the mass-spectrometric method for analyzing isotopes of oxygen in the form of carbon dioxide, a new standard was required, since abonding the former standard, water, made necessary presenting its oxygen in the form of carbon dioxide with the help of isotopic balancing, which results in relatively great isotopic fractionation. For experimental convenience, carbonates were used as a standard at first in many investigations, oxygen being liberated by treatment with anhydrous orthophosphoric acid. In this manner, however, only two thirds of the oxygen of the carbonate was liberated in the form of CO_2. It was found [8] that the oxygen in the liberated CO_2 was heavier than the total oxygen of the carbonate by about 1%. This introduced an inconvenience into the geochemical interpretation of the isotopic analyses of the oxygen of those natural materials, whose oxygen had been completely extracted for analysis, and required the application of a large correction, which exceeded by two orders of magnitude the accuracy of the experiment. Consequently, we, as well as certain other investigators [6, 7], selected pure quartz as a standard. The use of quartz as a source for standard oxygen is advantageous in that it has one of the highest O^{18}/O^{16} ratios for minerals and rocks. Moreover, the reduction of quartz by graphite begins at high temperatures. This assures ease in the operations preparatory to the reduction reaction, as well as a minimum experimental error. All determinations of isotopic ratios of oxygen separated from minerals and rocks in the form of CO were carried out in relation to carbon monoxide containing the oxygen of quartz.

Applicability of the Method

Clayton and Epstein, in their latest work, [8] consider reduction by graphite to be unsuitable for alumino silicate rocks containing alkali and alkaline-earth metals, and also Al and Zn. In reducing such rocks they did not obtain complete expulsion of CO or consistent results in isotopic analyses. They consider the instability of the carbides of these elements and the high vapor pressures of these metals at the experimental temperature to be the reasons for this. In the experiments of these investigators the carbides or metals volatized and escaped from the crucible, subsequently settled on the apparatus in the form of a mirror-like film and partially fixed the carbon monoxide being formed, thusly effecting a fractionation of the oxygen isotopes.

The volatility of the carbides of alkali and alkaline-earth metals and aluminum, and also of the metals themselves is well known, and at reduction temperatures they should be partially or completely sublimated from the solid residue. As well as can be estimated from a spectral analysis of the solid residue following reduction by graphite, practically all of the silicon, a substantial quantity of the iron (not less than 60%), about 12% of the calcium, and 6-7% of the aluminum still remains. The magnesium is sublimated in full. Table 5 (Note: The author thanks E. H. Savinova for performing the analyses.) presents an example of data characterizing the composition of the charge residue after reducing samples of dunite and diabase.

Table 5

Results of the Spectrographic Analysis of the Solid Residue Produced by the Reduction of Rocks by Graphite**

Element	Graphite	Experiment No. 46, dunite, "Polyarnyi Ural" Syum-Keu		Experiment No. 127, diabase, Noril'sk	
		Initial content of elements in the charge (in terms of the metal)	Solid residue after the reaction	Initial content of elements in the charge (in terms of the metal)	Solid residue after the reaction
Si	0.01	15.7	>10	13.2	>10
Mg	0.003	24.4	0.005	11.0	0.003
Al	-	0.3	0.02	4.6	0.3
Fe	0.005	4.0	3-5	8.0	3-5
Ca	0.0003	-	-	4.1	0.5
Cr	-	0.16	0.003	0.1	0.005

**The content of elements is given in percent.

The metal carbides vaporized from the combustion boat condense on the cold walls of the furnace only in a narrow band above the point of heating. Theoretically they can react partially at the surface with the CO, forming oxides again. However, this process, under the conditions selected for this experiment, is not of such a magnitude nor as important as described in [8]. In particular, the reverse reaction of CO with the carbides of metals is slowed by the dispersion of graphite from the point of heating on the graphite rod along this band on the surface of the furnace. It should also be noted that the duration of the reduction reaction in our experiments, i.e., the possible time of contact between CO and the sublimated carbides, is 12-18 min., whereas in [8], it is as much as 30-45 min. A two-minute exposure at each fixed temperature is quite sufficient. As many tens of experiments have shown, cessation of carbon monoxide liberation is noted on the manometer at the end of two minutes. The considerably greater quantities (5 times) of carbon monoxide obtained in our experiments as compared with [8] also decrease the importance of this effect.

Moreover, in conducting reduction experiments on even pure Al_2O_3 and MgO by graphite we obtained a CO yield of 96% of that theoretically possible in the case of Al_2O_3, and 82% for MgO (Fig. 5). A marked film adhered to the cold surfaces of the furnace only in the case of MgO. This is explained by the fact that the film consists predominantly of magnesium carbide. Consequently, the reverse reaction of fixating the oxygen of CO in the MgO is not observed under the conditions of the experiment. It is still less probable that such a reverse reaction would occur with the carbides of other metals.

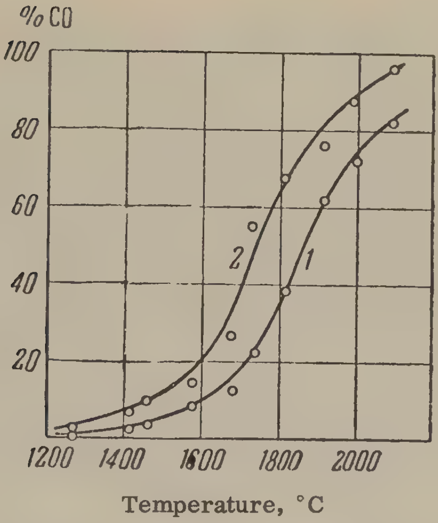

Fig. 5. Kinetic Curves of the Reduction by Graphite of Al_2O_3 and MgO 1-MgO; 2-Al_2O_3

Table 6

Average Relative Data on the Isotopic Analysis of Oxygen

Order	Material	Average deviation of O^{18}/O^{16} ratio of sample from standard %	Accuracy of experiment
1	Iron-stony meteorites (olivine fraction)	-0.70	±0.0
2	Stony meteorites (chondrites)	-0.68	±0.02
3	Stony meteorites (achondrites)	-0.64	±0.02
4	Ultrabasic rocks (dunites)	-0.62	±0.02
5	Basic rocks (basalts, diabases, and gabbro-diabases)	-0.46	±0.02
6	Acidic rocks (granites)	-0.16	±0.02

The sum total of data on the study of the kinetics of the reduction of rocks by graphite, the yield of carbon monoxide and its chemical analysis, and the reproducibility of mass-spectral isotopic analyses make it possible to conclude that the method is suitable for extracting oxygen from rocks and minerals (except carbonates) for purposes of isotopic analysis.

Utilizing this method a systematic study [1] was conducted to determine the relationships of oxygen isotopes in meteorites of different classes and in terrestrial rocks--ultrabasic, basic and acidic. In Table 6 average relative data on oxygen-isotope analyses for different kinds of meteorites and rocks are presented. Differences in the O^{18}/O^{16} ratio in these groups of rocks and meteorites lie far beyond the limits of the maximum experimental error. They make possible several general geochemical deductions.

Further investigations should be directed toward studying the distribution of oxygen isotopes, which may be influenced by different geochemical processes--such as magmatic differentiation, metamorphism, ore formation, and others--so that the oxygen isotope ratios observed in nature may be used to solve geochemical problems. This will require further improvement in oxygen-extracting methods, which are still not free from errors, and in methods of isotopic analysis.

REFERENCES

1. Vinogradov, A. P., E. I. Dontsova, M. S. Chupakhin. Geokhimya, No. 3, 187, (1958).
2. Manian, S. H., H. C. Urey, W. Bleakney. Amer. Chem. Soc. J. 56, 2601, (1934).
3. Bleakney, W. B., J. A. Hipple. Phys. Rev. 47, 800, (1935).
4. Vinogradov, A. P., E. I. Dontsova. Doklady AN SSSR 58, 83, (1947).
5. Baertschi, P. Nature 166, 112, (1950).
6. Baertschi, P., S. R. Silverman. Geochim. et Cosmochim. Acta 1, 317, (1951).
7. Schwander, H. Geochim. et Cosmochim. Acta 4, 261, (1951).
8. Clayton, R. W., S. Epstein. J. Geol. 66, 352, (1958).
9. Chupakhin, M. S. Zhurnal analiticheskoi khimii 14, 331, (1959).

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CONTRIBUTION TO THE PETROCHEMISTRY OF ULTRABASIC ROCKS

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(ABSTRACT)

In the article are given chemical analyses of ultrabasic rocks and stony meteorites of the USSR (300 analyses) recalculated for the modal mineral composition. The genetic groups of ultrabasic rocks: 1) hypermagbasites — derivatives of the peridotitic layer of the Earth (Sima): 2) ultraferbasites — differentiates of the gabbroic magma (Sialma) and 3) ultraalbasites — differentiates of the magma of alkaline gabbroids (Sialma), as well as stony meteorites have their definite numerical characteristics. It has been established that: 1) dunites of ultraferbasites and ultraalbasites have z = 100-95 and hypermagbasites z = 95-80, and, accordingly, peridotites z = z = 80-50 and z = 95-80; out of pyroxenites diallagites — kosvites are typical of ultraferbasites, websterites are typical of ultraalbasites and bronzitites of hypermagbasites (tabl. 6); 2) the formation of serpentinites at the expense of a definite variety of ultrabasic rocks and their belonging to one of the three genetic groups may be established according to the chemical composition; 3) in the process of serpentinization of the ultrabasic rocks an incarrying of SiO_2 — up to 2-3% is taking place; 4) in terrestrial ultrabasic rocks there practically are no varieties with ratios of olivine 50-15% and of pyroxenes 50-85; most of the stony meteorites have such a composition.

I. PETROCHEMICAL CHARACTERISTICS OF ULTRABASIC ROCKS AND DIAGRAMS OF THEIR CHEMICAL COMPOSITION

Ultrabasic rocks are widely distributed in the USSR. It has been shown that they include several genetic and age groups which are sometimes found together in a single region (the Urals, Caucasus). Ultrabasic rocks are often used to establish the age of other rocks by the presence of serpentinite pebbles and chromite grains in conglomerates and by the contact relationships with the rocks which enclose or cut them. More frequently, isolated outcrops of ultrabasic rocks, especially serpentinites, do not provide the geologist either with criteria for determining the relative age of other rocks or the age of the serpentinites themselves, nor with criteria for assigning them to a given genetic group or for determining the variety of the parent ultrabasic rock of the serpentinites.

Knowledge of the chemical composition of an ultrabasic rock makes it possible to determine the variety from which a given serpentinite was formed and the genetic group of both the serpentinite and the parent rock. The petrochemical characteristics of ultrabasic rocks provide an approach to the solution of some of the problems relating to ore deposits and the internal structure of the earth. Moreover, their chemistry may provide an answer to certain debatable questions of their own geology and petrography.

The petrochemical characteristics of the genetic types of ultrabasic rocks of the Caucasus were discussed by the author in an earlier paper [1]. According to A. N. Zavaritskii [2] there are three genetic types of ultrabasic rocks: a) the independent large peridotite bodies, believed to have been intruded as the result of especially deep subsidences of the crust and having their roots in the sima; b) the extreme differentiates of gabbroic magma, which are also localized in the geosynclinal belts and are related, according to T. Barth [3], to the sialma shell; and c) the ultrabasic rocks related to the alkalic gabbroic magmas associated with carbonatites. The latter are found in the platform regions (Kola Peninsula, Siberian Platform, Aldan) and are most frequently represented by intrusions of the central vent type. These three genetic types were named by the author [4]: the hypermagbasites with $MgO:FeO^{-} = 9 - 10$; the ultraferbasites, with $MgO:FeO^{-} = 5 - 6$; and the ultraalbasites, whose petrochemical characteristics have not been determined as yet.

It is possible now to generalize the data on the chemical composition of the ultrabasic rocks of the Caucasus, the Urals, Kola Peninsula, Western Sayan and Altai, Eastern Sayan and Central Kazakhstan. These generalizations are based on about 300 chemical analyses, partly selected from two collections of chemical analyses of rocks compiled by Z. N. Nemova [5] and E. A. Struve [6], and partly collected by the author from the publications of the last twenty years. The generalizations are made by comparing the chemical composition diagrams constructed by Zavaritskii's method [7, 8] and modified by the author [1] especially for the ultrabasic rocks by replacing the characteristics c', f', m', n by x, y, z and h. These modifications have justified themselves in practice and have been approved by a number of geologists--K. N. Paffengol'ts, G. V. Pinus and others [9, 10].

The modifications consist in recalculating the analyses to normative olivine (z), orthopyroxene (y) and clinopyroxene (x) and representing them by vectors on the right side of the diagram and in showing the degree of serpentization (h) by vectors on the left side of the diagram [1].

In addition to these modifications in the numerical characteristics and the composition diagram for the ultrabasic rocks, two more changes are proposed here. The feldspars being absent from ultrabasic rocks, Zavaritskii's characteristics a and c [7] cannot be used, and thus all composition points will lie on the straight line S. The vacant right side of the diagram can be utilized to show the genetic groups of ultrabasic rocks by plotting on it the $MgO:FeO^{-}$ ratios. To do this, the sum of the oxides of the oxides of the iron group elements ($FeO + Fe_2O_3 + MnO + NiO$) is

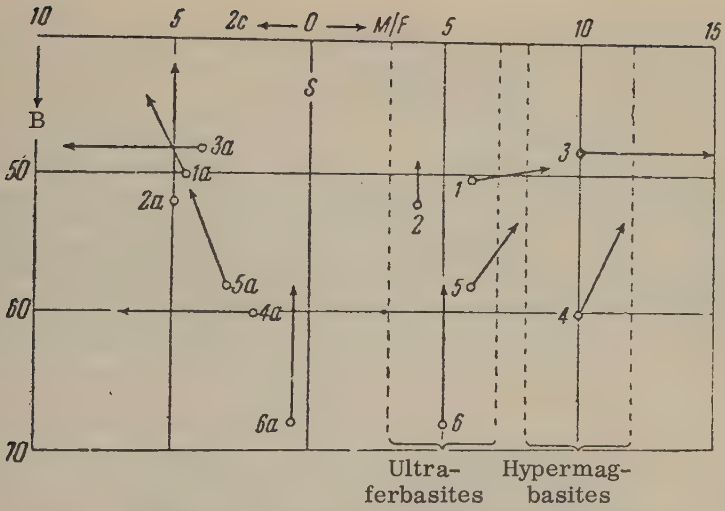

Fig. 1. Diagram of chemical composition of ultrabasic rocks

1 - websterite, 2 - koswite-diallagite, 3 - bronzitite, 1a - serpentinized websterite, 2a - unserpentinized koswite, 3a - apobronzitite serpentinite, 4 - harzburgite, 5 - lherzolite, 6 - dunite, 7 - apoharzburgite serpentinite, 5a - serpentinized lherzolite, 6a - unserpentinized dunite

equated to unity and the above ratios are designated M/F (part of MgO + FeO must first be assigned to the chrome spinels). The left side of the diagram may be used to show the contribution to the composition of ultrabasic rocks by chrome spinels denoted by 2c (double the molecular amount of the sum of aluminum and chromium oxides). These changes are illustrated by a recalculation of a chemical analysis of peridotite (Table 1) and the chemical composition diagram of ultrabasic rocks (Fig. 1).

The right side of the diagram is ferromagnesian and the position of the composition points on it indicates to what particular genetic group a given sample belongs, each of the groups being characterized by a definite value of M/F. The length and direction of a vector shows what particular variety of ultrabasic rock the sample is associated with: the long vertical vectors indicate dunite, the short--koswite-diallagite; the long horizontal vectors indicate bronzitite, the short--websterite; the long inclined vectors indicate harzburgite-saxonite, the short--lherzolite, wehrlite. The numbers at the ends of the short inclined vectors show the value of the auxiliary characteristic "x", i. e. the relative amount of normative diopside.

The left side of the diagram is for the spinels, and the position of the composition points on it shows the relative amount of the spinels in the rocks, each main variety of ultrabasic rocks, dunites, peridotites and pyroxenites being characterized by a definite numerical value of 2c. The direction of the vectors on the left side of the diagram shows the degree of serpentinization of the ultrabasic rock: the vertical vectors indicate unserpentinized rock, the inclined, serpentinized rocks, and the horizontal,

Table 1

	Weight %	Mol. amount		
SiO_2	41,18	686		687—S
TiO_2	0,06	1		
Al_2O_3	1,80	18		×2=42—2c
Cr_2O_3	0,50	3		
Fe_2O_3	3,51	22	×2=44	1116—B
FeO	5,39	75	—3=72	
MnO	0,12	1		
MgO	41,18	997	—18=979	
CaO	1,32	20		

$$2C=42 \qquad 2c=2{,}3$$
$$S=687 \qquad s=37{,}2$$
$$B=1116 \qquad \mathit{в}=60{,}5$$
$$\overline{1845 \qquad\qquad 100{,}0}$$
$$h=\frac{Fe_2O_3\times 100}{Fe_2O_3+FeO}=22{,}4$$
$$x+y+z=B-1116$$
$$x+y+\frac{z}{2}=S-687$$
$$x=2CaO-40$$
$$\frac{z}{2}=429;\; z=858;\; y=218$$

	SiO_2	(Mg, Fe)O	CaO	Mol. amt.	Numer. char.
z	429	858	—	1287	71,4
x	40	20	20	80	4,5
y	218	218	—	436	24,1
	687	1096	20	1803	100,0

$$M/F=\frac{MgO}{FeO+2Fe_2O_3+MnO+NiO}=\frac{979}{117}=8{,}4$$

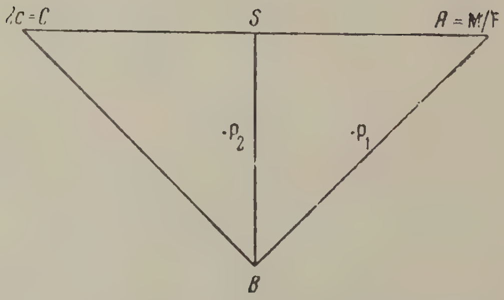

Fig. 2. Figurative points of the main numerical characteristics projected from a three-dimensional diagram on the developed planes SAB=SM/FB and SCB=S2cB

serpentinites*.

Zavaritskii's diagrams are projections of a tetrahedron on a plane with the coordinate axes (Fig. 2): SA, the alkali axis; SC, the anorthite axis; and SB, the femic axis. Two compositional points (P_1 and P_2) determined by the main numerical characteristic (i. e., $\underline{a}+\underline{c}+\underline{b}+\underline{s} = 100$) are projected on this plane.

In the diagrams of ultrabasic rocks, the alkali axis is replaced by the ferromagnesian axis (M/F), the anorthite axis, by the spinel axis (2C) and the femic axis is retained.

The auxiliary characteristics are represented by a point in a triangle whose scale is 1/10 of the scale of the diagram of the principal numerical characteristic. If the side of the triangle (Fig. 3) is 100 and $\underline{f}' + \underline{m}' + \underline{c}' = 100$, then $\underline{f'R} = \underline{c}'$, $\underline{PR} = \underline{m}'$ and $\underline{PU} = \underline{f}'$. In our diagrams, the auxiliary characteristics are modified as follows. The molecular amounts in the chemical analysis of an ultrabasic rock are recalculated by means of the equations:

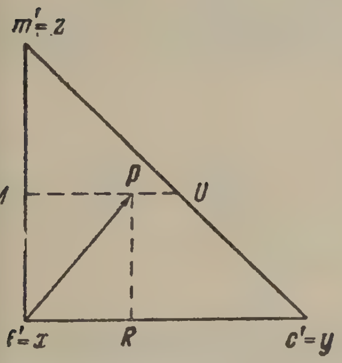

Fig. 3. Construction of auxiliary characteristics $\underline{c}' : \underline{m}' : \underline{f}' = \underline{y} : \underline{z} : \underline{x}$

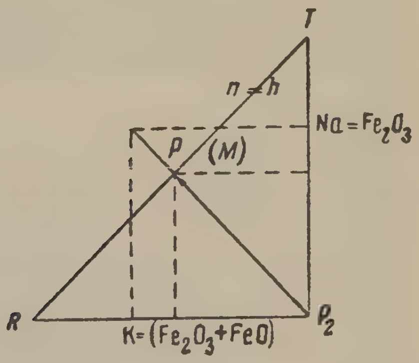

Fig. 4. Construction of auxiliary characteristic $\underline{n} = \underline{h}$

$$\underline{x} + \underline{y} + \underline{z} = MgO + FeO + 2Fe_2O_3 + CaO \qquad (1)$$

$$\underline{x} + \underline{y} + \underline{z}/2 = SiO_2 \qquad (2)$$

$$\underline{x} = 2CaO \qquad (3)$$

---

*In accordance with the opinion of P. M. Tatarinov [11], D. S. Belyankin (see Winchell's Optical Mineralogy, 1953, p. 496), and A. N. Zavaritskii [2], the word zmeevik should be used instead of serpentinite.

where the molecular amount of SiO_2 is distributed among the clinopyroxenes -- x, the orthopyroxenes -- y, and the olivines -- $z/2$. After adding appropriate amounts of bases to silica to form ortho-pyroxene, clinopyroxene and olivine, designated x, y and z, respectively, the sum of the molecular amounts of these minerals is recalculated to 100. Zavaritskii's auxiliary characteristics are replaced as follows: $m' = z$, $c' = y$ and $f' = x$, and are plotted as vectors on the right side of the diagram (Fig 2 and 3).

Another auxiliary characteristic is the ratio n = Na: (Na + K). It may be represented by the direction of a line dividing the angle between two other lines.

The values proportional to K and Na are plotted on the mutually perpendicular axes P_2R and P_2T (Fig. 4). The direction of line P_2P uniquely defines the Na:K ratio, and therefore n. If a right equilateral triangle, P_2RT, is drawn, it becomes clear (Fig. 4) that $RM:MT$ = Na:k and $RM:RT = n$ expressed in per cent.

For ultrabasic rocks n = Na: (Na+K) is replaced by $h = Fe_2O_3:(Fe_2O_3 +$ FeO), which is shown by a vector on the right side of the diagram.

On the basis of diagrams constructed in this manner, we shall discuss the actual material from the mountain regions named above.

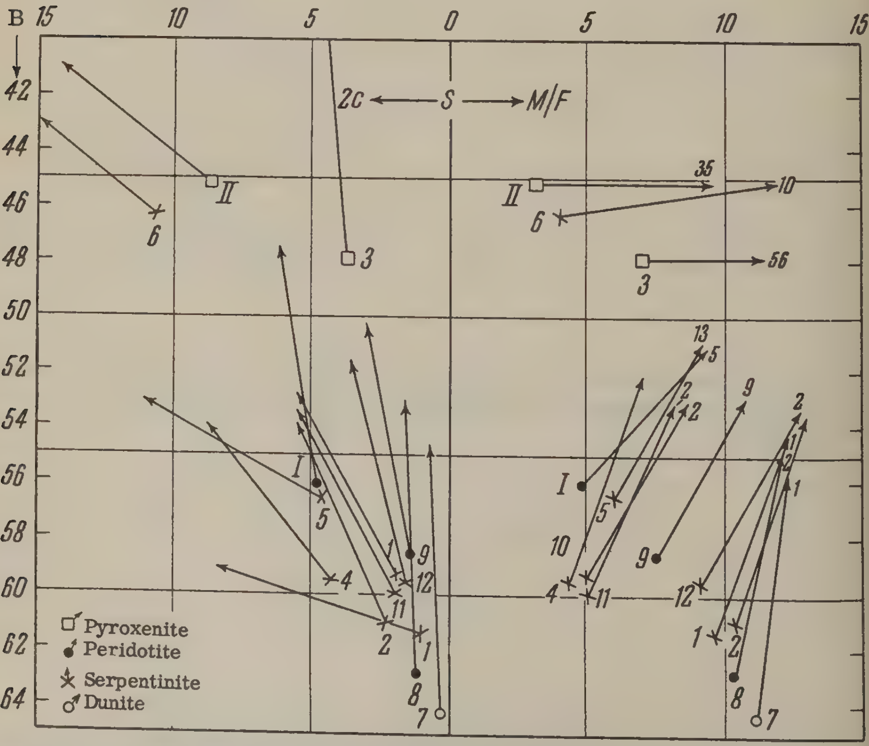

Fig. 5. Chemical composition diagram of Proterozoic hypermagbasites and ultraferbasites of the Caucasus

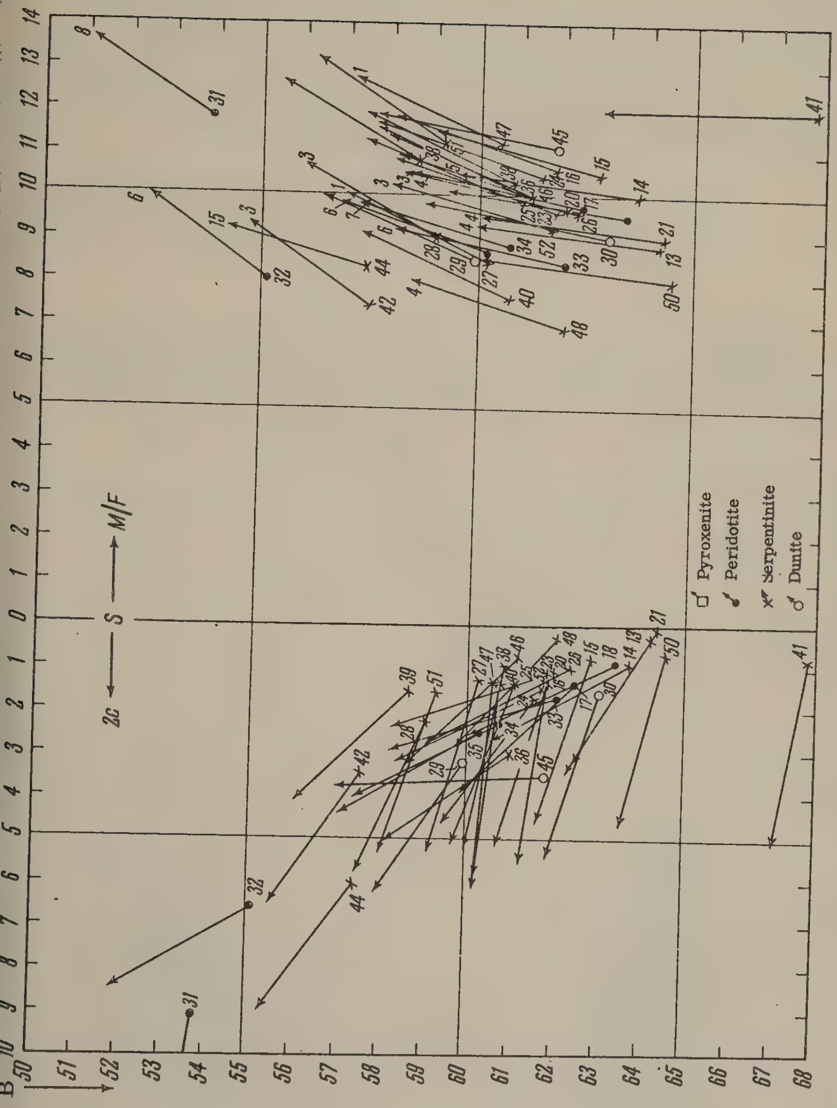

Fig. 6. Chemical composition diagram of Middle Paleozoic hypermagbasites of the Caucasus

2. PETROCHEMISTRY OF THE GENETIC AND AGE GROUPS OF ULTRABASIC ROCKS OF THE USSR

The Caucasus. It has been shown [1] that here there are three age and genetic groups of ultrabasic rocks: 1) the Proterozoic hypermagbasites (6 analyses, Fig. 5); 2) the Proterozoic ultraferbasites (8 analyses, Fig. 5) and 3) the Middle Paleozoic hypermagbasites represented by peridotite massifs (35 analyses, Fig. 6). It follows from the diagrams that each group has a definite numerical characteristic M/F and Table 2 shows that the component rocks have similar numerical characteristics.

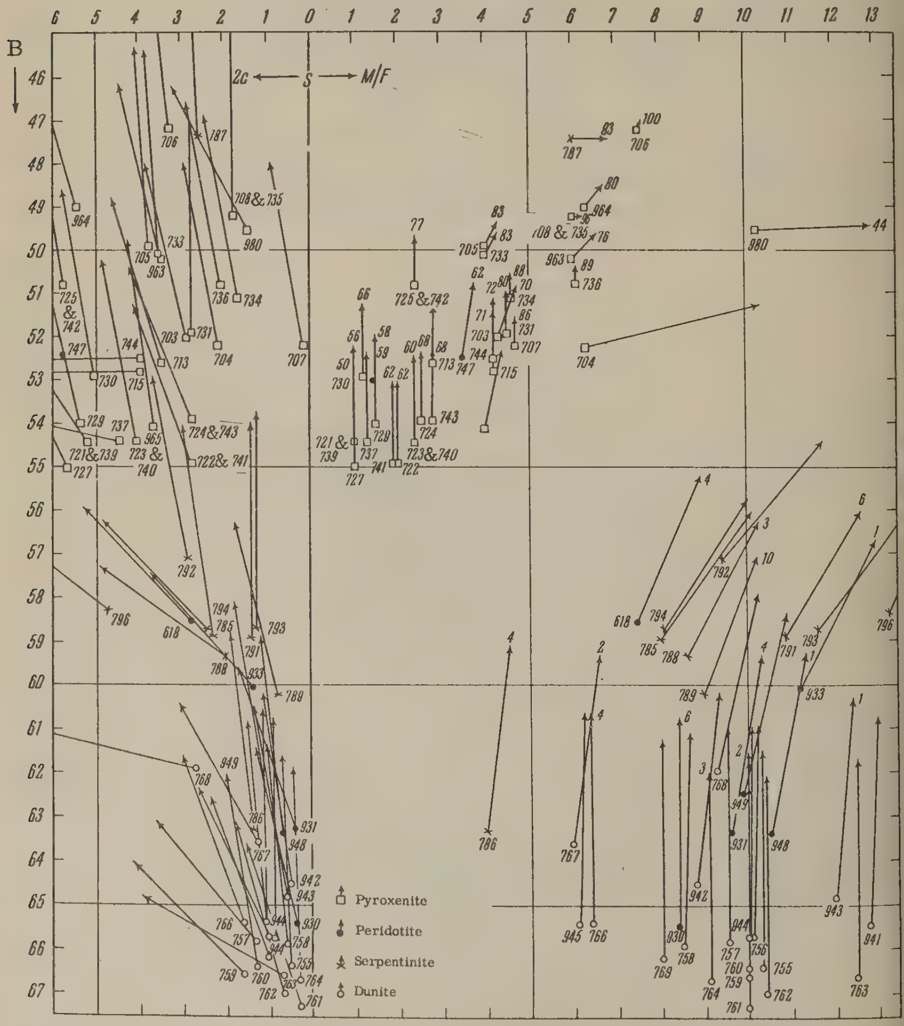

Fig. 7. Chemical composition diagram of Lower Paleozoic ultraferbasites of the western belt of the Urals

Table 2

Group	M/F	Rocks	b	2c
Hypermagbasite — – Proterozoic	8–11	Peridotites Dunites	58–63 63–65	1–3 0–1
Ultraferbasite — – Proterozoic	3–7	Pyroxenites Peridotites	45–48 56–60	4–11 1–5
Hypermagbasite — – Middle Paleozoic	8–12	Peridotites Dunites	54–62 62–68	2–4 0–1

The Urals. According to the data of G. L. Padalka [12], P. M. Tatarinov 11] and V. M. Sergievskii [13], there are at least two age and genetic roups of ultrabasic rocks in this region: 1) the Lower Paleozoic ultra-erbasites, differentiates of gabbroic magma in the well-known platinum

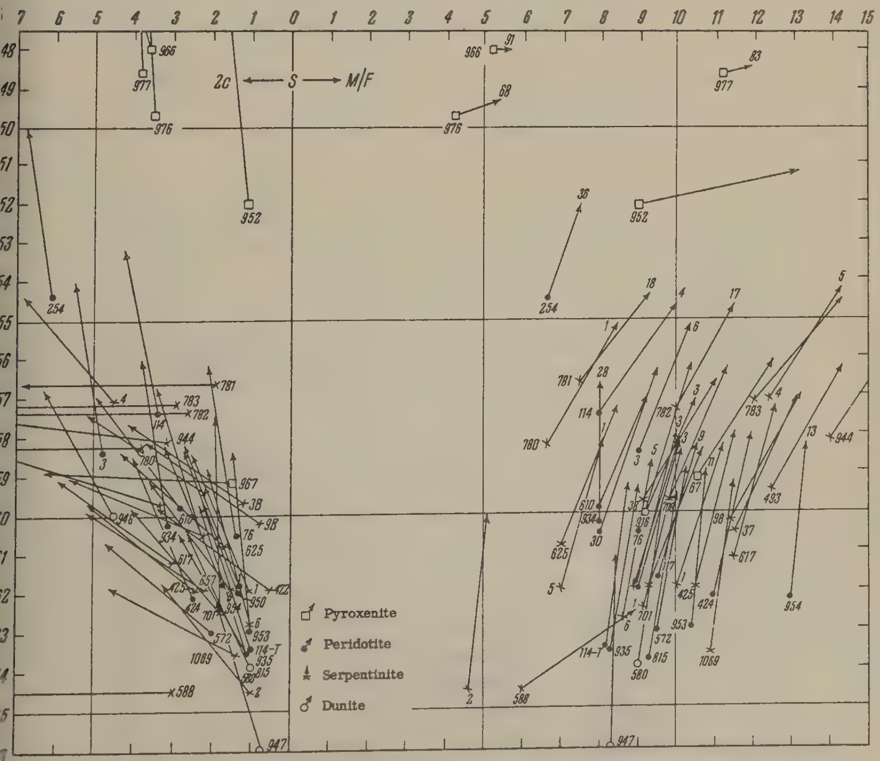

Fig. 8. Chemical Composition Diagram of Middle Paleozoic hypermagbasites of the Central and Eastern Belts of the Urals

Table 3

Group	M/F	Rocks	b	2c
Ultraferbasite-Lower Paleozoic, western	2-6 in pyroxenites, 6-13 in dunites and peridotites	Pyroxenites Peridotites Dunites	47-55 58-63 63-67	2-6 1-3 0-2
Hypermagbasite-Middle Paleozoic, eastern	6-13	Pyroxenites Peridotites Dunites	48-53 56-63 63-66	1-4 2-5 1-2

belt of the Urals (68 analyses, Fig. 7) and 2) the Middle Paleozoic hypermagbasites, asbestos and chromite-bearing peridotite massifs of the central and eastern belts of the Urals (48 analyses, Fig. 8). The data of the two diagrams are compared in Table 3.

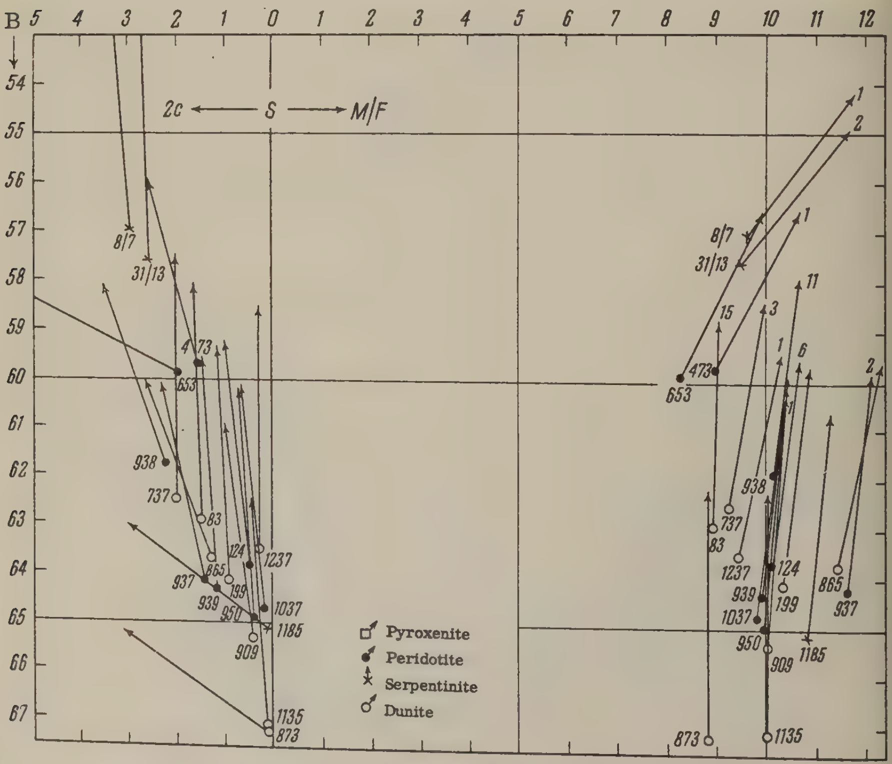

Fig. 9. Chemical Composition Diagram of Lower Paleozoic hypermagbasites of Eastern Sayan

The hypermagbasites of the Urals and the Caucasus agree in all numerical characteristics, but the M/F characteristic of the Uralian ultraferbasites, while the same for the pyroxenites of both regions, shows a greater range of variation in the Uralian peridotites and dunites (6-13). This peculiarity can probably be explained by the fact that in the western belt, especially in the extreme west, there are Middle Paleozoic ultrabasic massifs (so-called small intrusions) which, as was pointed out by G. L. Padalka [12] and also by P. M. Tatarinov [13], resemble hypermagbasites. It may be supposed, therefore, that among the chemical analyses of the ultrabasic rocks of the western belt of the Urals both genetic and age groups are present which cannot be separated at present for lack of data.

Eastern Sayan. As has already been shown by the author [14], this region contains only Lower Paleozoic ultrabasic massifs of the hypermagbasite type (19 chem. analyses, Fig. 9) and they agree in all characteristics with the hypermagbasites of the Caucasus and the Urals.

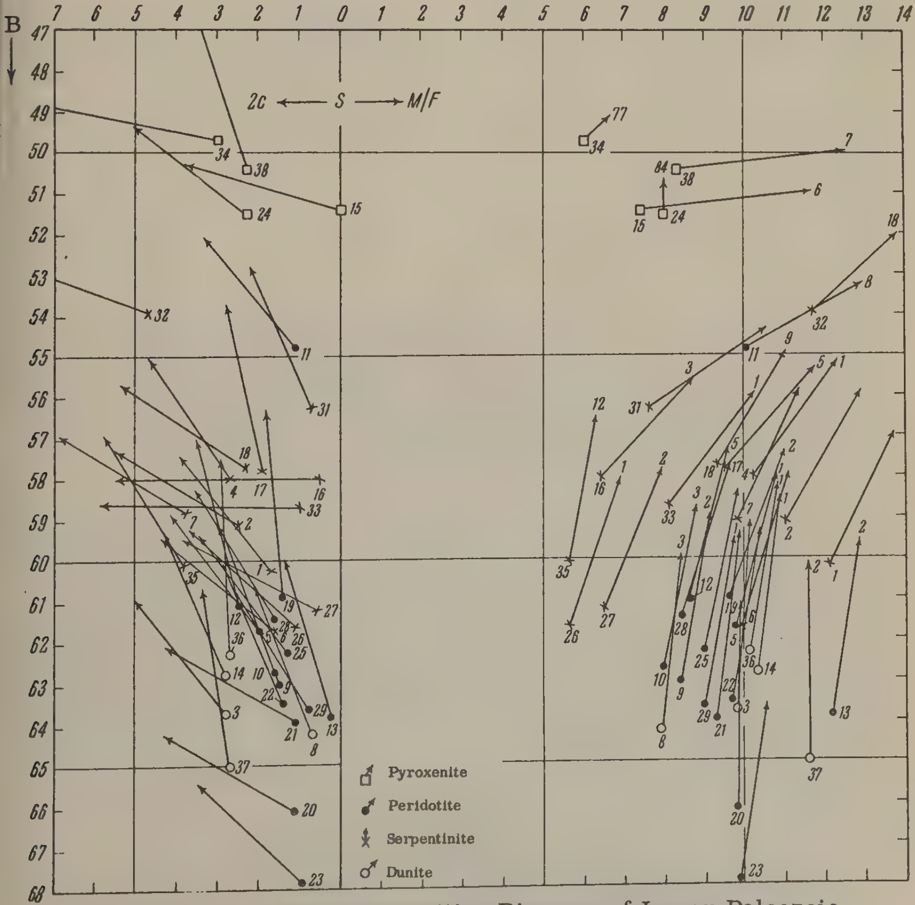

Fig. 10. Chemical Composition Diagram of Lower Paleozoic Hypermagbasites of Western Sayan and Altai

Western Sayan and Altai. According to the data of G. V. Pinus, V. A. Kuznetsov and I. M. Volokhov [15] and M. I. Yudin [16], there are Lower Paleozoic ultrabasic massifs in these regions represented by hypermagbasites (38 chem. analyses, Fig. 10), which with few exceptions, agree in all characteristics with the rocks of this type in the Caucasus, the Urals and Eastern Sayan.

Central Kazakhstan. According to N. P. Mikhailov [17], the ultrabasic massifs of this region are all of the same pre-Caradoc age and all are hypermagbasites, in some cases intimately related to gabbro (23 chem. analyses, Fig. 11). However, the diagram shows clearly that there are representatives of two genetic types in this region, with M/F = 4-6.5 and M/F = 8-12, which cannot be of the same age. The geologists of Kazakhstan are faced with the problem of separating the massifs into ultraferbasitic and hypermagbasitic and determining the age of each of these groups.

Kola Peninsula. The ultrabasic rocks of this region have been studied by B. M. Kupletskii, O. A. Vorob'eva, N. A. Eliseev, N. D. Sobolev and others. They represent the third group, the ultraalbasites, or differentiates of the ultraalkalic magma (38 chem. analyses, Fig. 12). All numerical characteristics of these rocks coincide with those of ultraferbasites, and therefore they may be regarded as the products of the sialma.

Table 4

Rocks	b	2c
Pyroxenites	40-56	3-13
Peridotites	56-62	2-5
Dunites	62-68	0-2

The following conclusions may be drawn from the petrochemistry of ten genetic and regional groups of the ultrabasic rocks of the USSR:

1) The principal varieties of ultrabasic rocks have like numerical characteristics independent of their membership in one of the genetic groups.

These characteristics permit determination of the parent rock of a given serpentinite. They indicate, moreover, that chromite deposits are associated with peridotites and not with dunites, because the former have a higher content of chrome spinel (2c). Pyroxenites also have high values of characteristic 2c, but they occur as small masses, veins, schlieren and borders, and cannot be expected to contain chromite ore bodies.

2) The three genetic types of ultrabasic rocks have definite characteristics: in the hypermagbasites M/F = 8-12; in the ultraferbasites and ultraalbasites M/F = 4-7. Using this characteristic, an individual ultrabasic massif may be referred to a definite genetic group. The identity of the characteristic in the last two groups is of no significance for this purpose, because the two types, so far as is known, do not occur in the same region. Moreover, these two groups are sharply distinguished by their pyroxenites. In the ultraferbasites these rocks are koswites and diallagites (short vertical vectors in Fig. 7), while in the ultraalbasites they are websterites (horizontal vectors, Fig. 12).

3) In the USSR ultrabasic rocks are more or less widespread in the following regions:

1. In the Ukraine -- ultraferbasites of uncertain age.
2. In Transcaucasia--Mesozoic hypermagbasites.
3. In the Pamirs and T'ien Shan.
4. In the northern part of the Siberian platform--ultraalbasites of uncertain age.

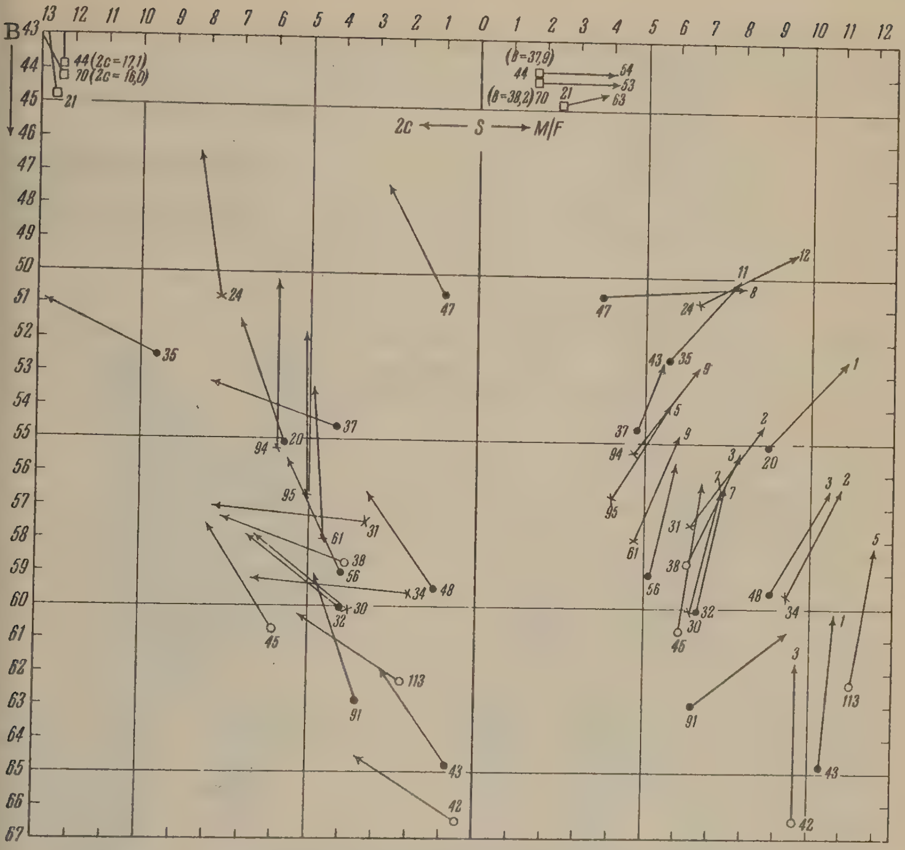

Fig. 11. Chemical Composition Diagram of Lower Paleozoic and Proterozoic (?) Hypermagbasites and Ultraferbasites of Central Kazakhstan

5. In Transbaikalia--Lower Paleozoic hypermagbasites.
6. On the Aldan plateau--Mesozoic ultraalbasites.
7. On Kamchatka, the Kurile Islands and Sakhalin--Mesozoic hypermagbasites.

Although necessary materials from these regions are lacking at present, they will be analyzed in the future. As can be seen from the example of Central Kazakhstan, a study of petrochemistry of the ultrabasic rocks of these regions will contribute to the objective solution of a number of difficult geological problems.

4) Figs. 13-17 were drawn to determine the range of chemical composition of ultrabasic rocks and the gradations between dunites, peridotites and pyroxenites, to discover which of these rocks are most susceptible to serpentinization, and, finally, to determine the role played in them by normative diopside. In these figures all points on the right side of the composition diagrams (Figs. 5-12) are shifted to one point and all vectors showing

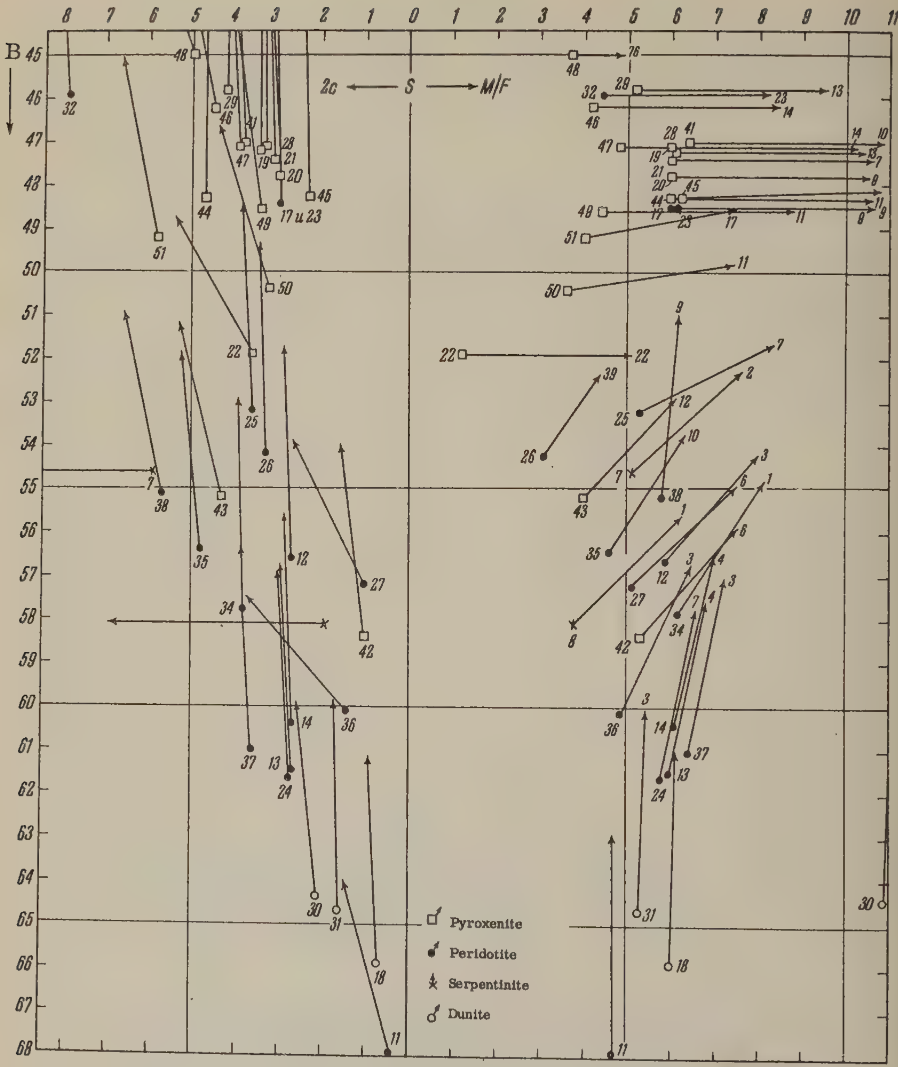

Fig. 12. Chemical composition diagram of ultraalbasites of Kola Peninsula

the actual mineralogical composition are plotted. The grouping into dunites, peridotites, pyroxenites and serpentinites is given in accordance with determinations by the authors who described the rocks so that these diagrams are, in effect, a "poll" of what most petrographers understand by these names. It is important to clarify this point, because, as Loewinson-Lessing has shown [18], there is no agreement among petrographers even on the composition of dunite.

The data of Fig. 13 show that, as Loewinson-Lessing pointed out, it is

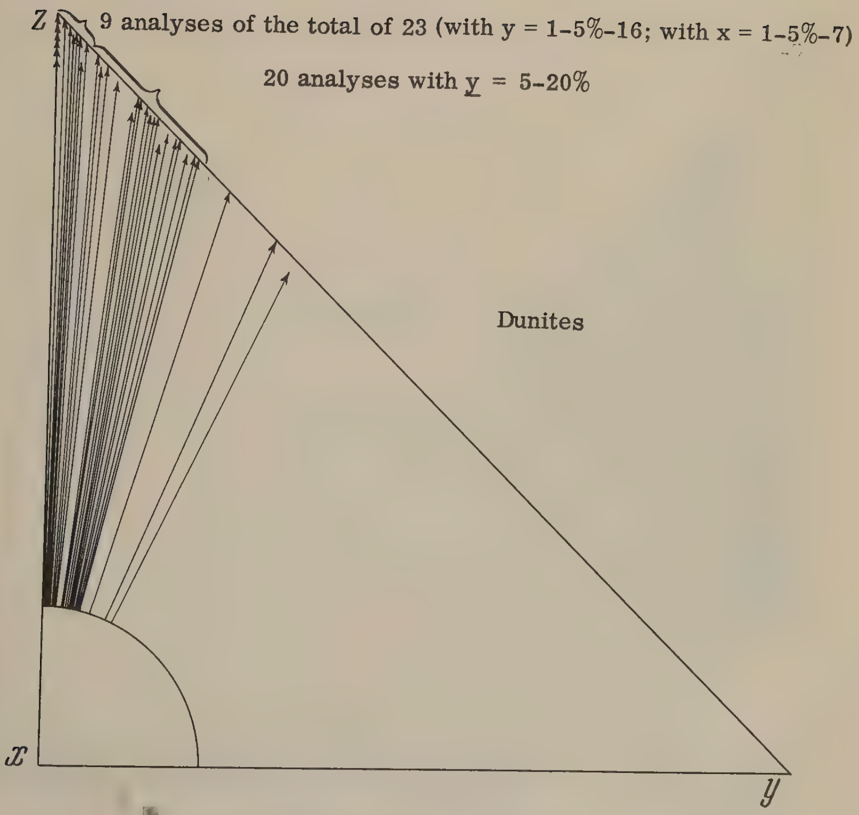

Fig. 13. Normative mineral composition of dunites of the USSR

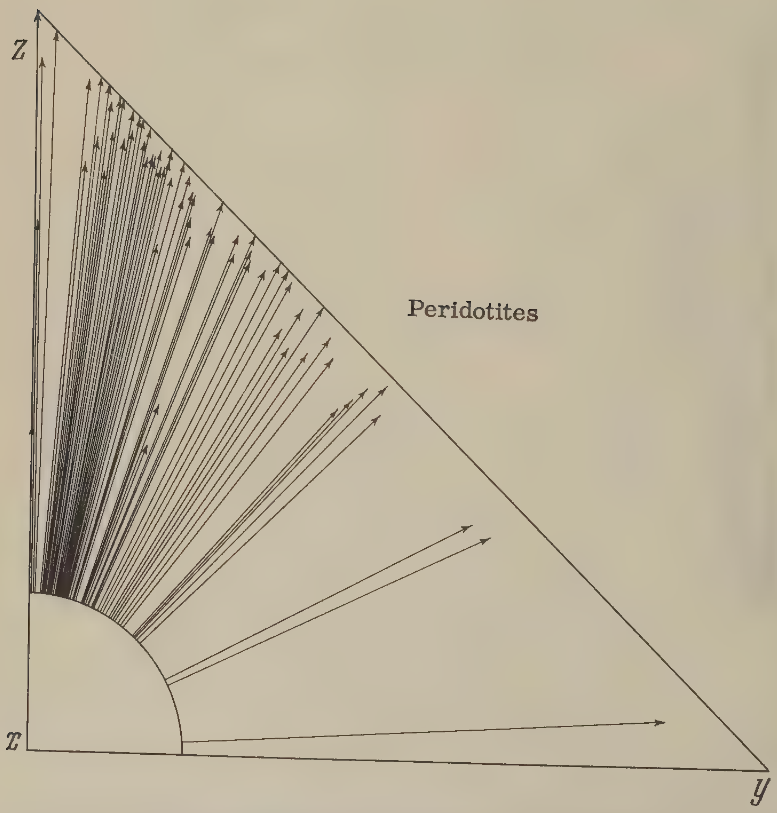

Fig. 14. Normative mineral composition of peridotites of the USSR

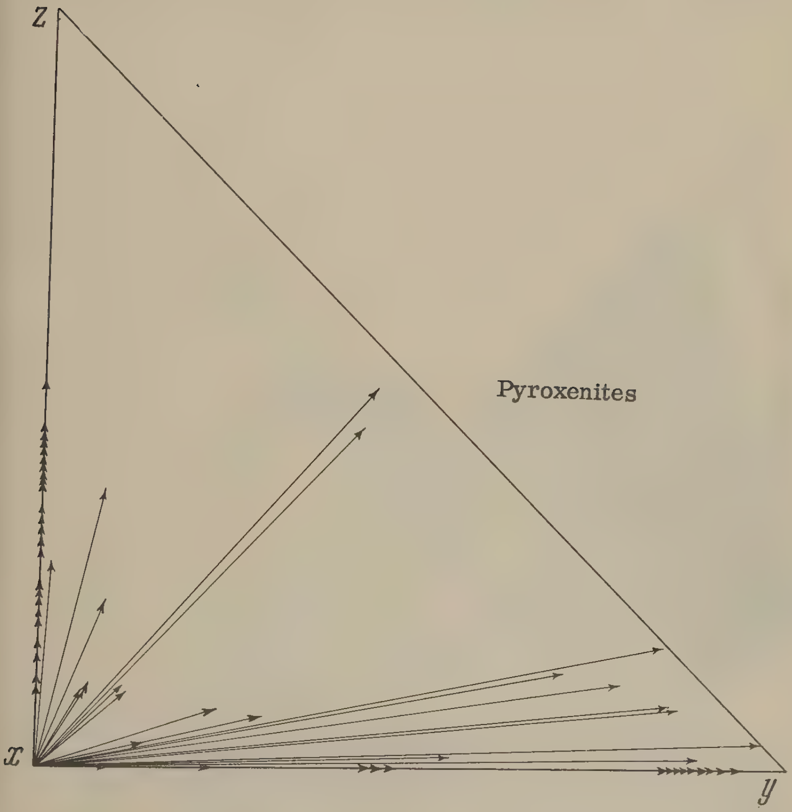

Fig. 15. Normative mineral composition of the pyroxenites of the USSR

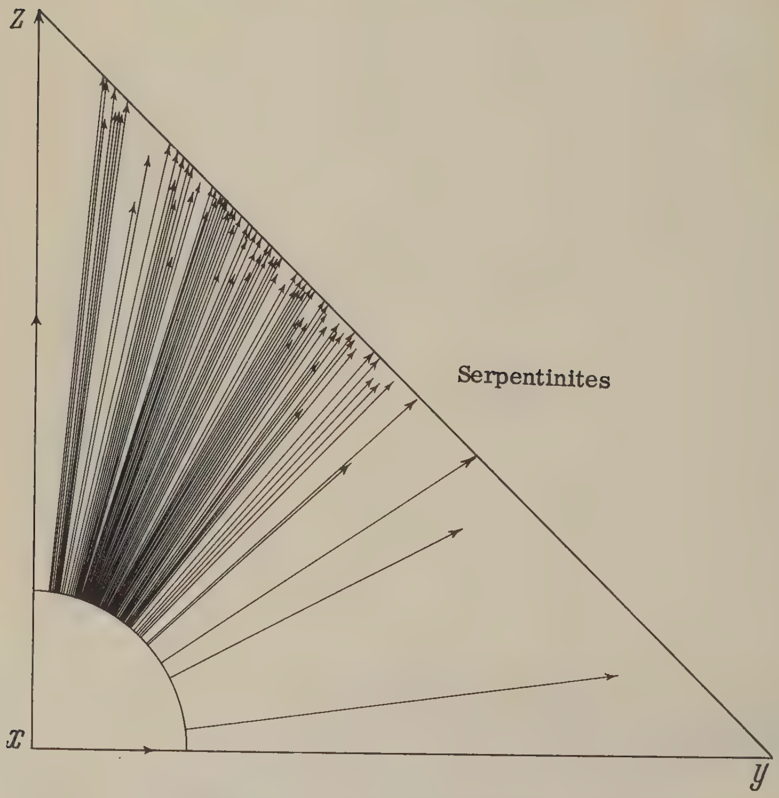

Fig. 16. Normative mineral composition of the serpentinites of the USSR

necessary to distinguish dunites proper, containing from 0 to 5% enstatite. Twenty three analyzed dunites fall into this group, and in seven of the analyses, diopside is present instead of enstatite (probably diallage or augite). In the overwhelming majority of cases (20 analyses), these dunites belong to the ultraferbasite and ultraalbasite groups. The second group is represented by enstatite dunites with 5 to 20% enstatite (20 analyses), some of them also containing up to 5% diopside. In most cases (18 analyses) the enstatite dunites are hypermagbasites.

According to their chemical composition, the 81 analyzed peridotites (Fig. 14) are distributed as shown in Table 5.

It follows from the data of Figs. 13 and 14 that the petrographers who have studied ultrabasic massifs of the ultraferbasite and ultraalbasite types have named rocks containing 0–5% enstatite as dunites and those with

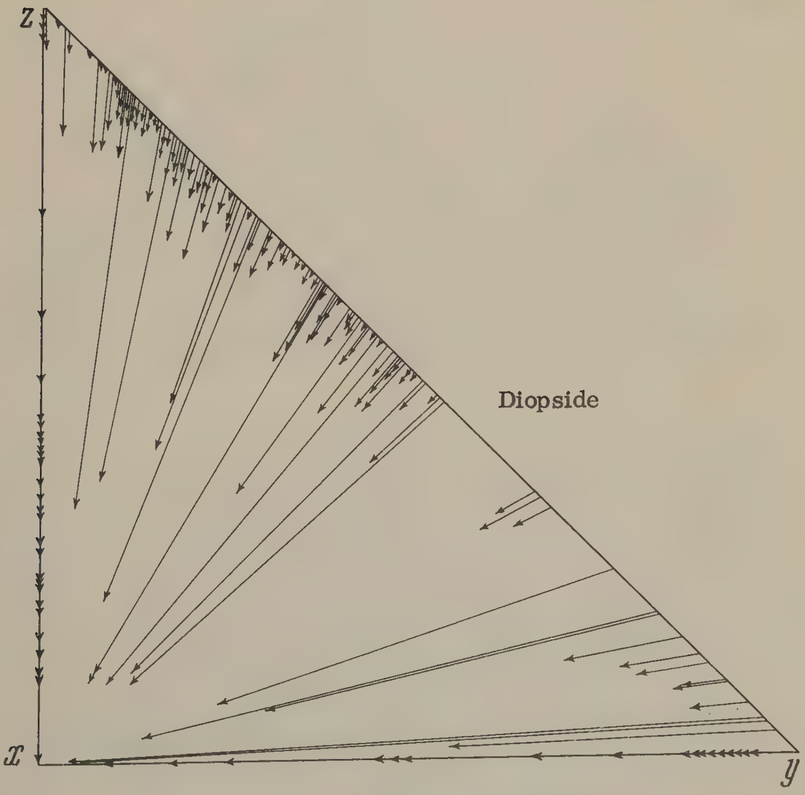

Fig. 17

Fig. 17. Normative diopside in the ultrabasic rocks of the USSR

a – ultraferbasite and ultraalbasite dunites, b – hypermagbasite dunites and peridotites, c – ultraferbasite and ultraalbasite peridotites, d – stony meteorites, e – pyroxenites

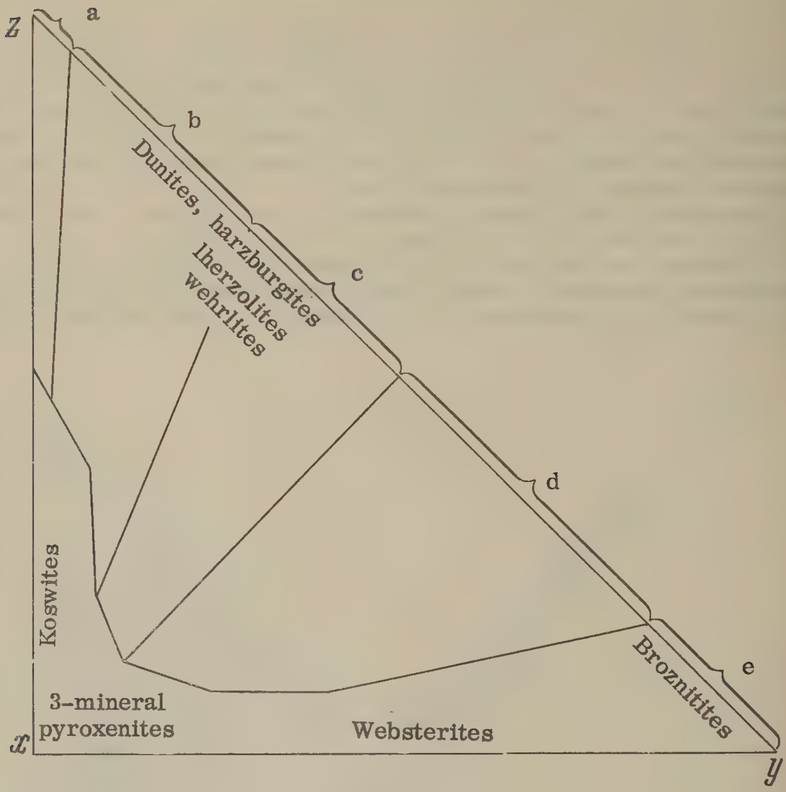

Fig. 18

Table 5

Number of analyses	% enstatite	Analogues	Group
3	–	Koswites	Ultraalbasites, ultraferbasites
3	0–5	Dunites	"
53	5–20	Peridotites	Hypermagbasites
18	20–50	Peridotites	Ultraalbasites, ultraferbasites
4	50–100	Pyroxenites	Ultraalbasites

20-50% enstatite as peridotites; i.e. there is a tendency in these types of rocks to a sharp isolation of olivine into monomineralic rocks (gap in $\underline{y}$ = 5-20%).

The petrographers who have studied ultrabasic massifs of the hypermagbasite type derived from magma which did not tend to differentiate into mono- and bimineralic rocks, attempted to separate rocks with 5 to 20% of enstatite into dunites and peridotites. In this group there are no dunites with an enstatite content of 0-5%. This is typical of the ultraferbasites and ultraalbasites, which are also characteristically differentiated into gabbro, monomineralic olivine rocks and pyroxenites and bimineralic peridotites. Thus, attempts were made to fit hypermagbasitic dunites into the ultraferbasitic with a different olivine-pyroxene ratio.

The 63 analyzed pyroxenites (Fig. 15) fall into three distinct groups listed in Table 6.

Table 6

Number of analyses	Pyroxenites	Group
36	Koswites, diallagites	Ultraferbasite
17	Websterites	Ultraalbasite
10	Bronzitites	Hypermagbasite

All groups show a tendency to contain three minerals, olivine, clinopyroxene and orthopyroxene, one of the pyroxenes predominating.

The chemical analyses of serpentinites (93 analyses) are plotted in Fig. 16, which shows clearly that all varieties of peridotites are susceptible to serpentinization but especially harzburgites. Diagrams 14 and 16 indicate hat in serpentinization hydrothermal solutions introduce a small amount of silica. If silica were removed, most serpentines would correspond to dunites in composition. It is well known that dunites may be completely serpentinized (although less commonly than peridotites) but they are absent rom Fig. 16, which contains only peridotites with a minimum value of y = 9 (i.e. with 9% normative enstatite). The other boundary of peridotites also indicates addition of silica. The maximum value of $\underline{y}$ is 50 in unserpentinized peridotites and 60 in the serpentinite. Thus, it follows definitely rom both boundaries that in serpentinization there is an addition of silica, which increases the amount of normative enstatite by 5-10%. This is learly shown by the extreme left vector bundle of serpentinites formed rom dunites (8 vectors). For the majority of vectors, $\underline{y}$ = 20-60, while in the unserpentinized peridotites $\underline{y}$ = 10-50. The debatable petrographic question whether silica (and also magnesia) is added or subtracted in serpentinization is solved definitely by petrochemistry.

The ultrabasic rocks of the ultraferbasite (7 analyses) and ultraalbasite types (3 analyses) are very seldom serpentinized. Of the total of 90 analyses of serpentinites, 80 are of the rocks of the hypermagbasite type.

Figs. 13-16 show that there are practically no ultrabasic rocks with y = 50-85, i. e. rocks intermediate between peridotites and pyroxenites (bronzitites, websterites), and this, as will be shown later, is a very characteristic difference between terrestrial ultrabasic rocks and stony meteorites.

Fig. 17 shows another bundle of short vectors plotted in Figs. 5-12, which represent the relative amount of normative diopside in the composition of more than 200 analyzed ultrabasic rocks. According to the diagram: a) diopside is present in all ultrabasic rocks, b) the shortest vectors represent its role in the composition of harzburgites, c) the somewhat longer vectors--in therzolites, d) the still longer ones, in wehrlites, and, finally, e) the longest vectors reflect the participation of diopside in the three-mineral pyroxenites--the olivine websterites.

The chemical data for the ultrabasic rocks of the USSR are generalized in Fig. 18, which shows clearly both the petrochemical characteristics of each group and the differences in the mineralogy of the varieties of ultrabasic rocks. The diagram shows also the generalized data on stony meteorites which are discussed below.

3. PETROCHEMICAL CHARACTERISTICS OF TERRESTRIAL ULTRABASIC ROCKS AND STONY METEORITES

If our concepts of the internal structure of the earth are correct, then it follows from the principles of gravity differentiation that the amount of iron must increase from the sialma towards the earth's iron core, and accordingly the fayalitic and ferrosilitic components must increase with depth in the peridotitic shell of the sima. In reality, we have the relations reversed; i. e., in the sialma derivatives, ultraferbasites, M/F = 4-7, while in the sima derivatives, hypermagbasites, M/F = 8-12. Thus, either these derivatives are incorrectly assigned to these shells of the earth, or there is a pattern of distribution here which is still obscure. Judging by the opinions of Zavaritskii and Kvash [19], the latter hypothesis is correct, for the orthopyroxene in the stony meteorites is either iron-free enstatite or bronzite and hypersthene (12-25% FeO) and the olivine is chrysotile (11-13% FeO), i. e. minerals characteristic of hypermagbasites.

It was stated by A. P. Vinogradov [20] that in order to clarify these and other questions it is necessary to use the petrochemical data on stony meteorites, but always keeping in mind that the analyses of their silicate phases show an iron content slightly higher than the actual, because of the difficulty of separating the silicate fraction from the meteoritic iron. Below, certain comparisons will be made between the petrochemistry of terrestria ultrabasic rocks and feldspar-free stony meteorites. For this purpose, a diagram has been constructed after the data of Zavaritskii and Kvasha [19], which shows that the majority of meteorites have M/F - 1-4, and a maximum of 7; i. e., among the stony meteorites there are no analogues of terrestrial ultrabasic rocks. This is confirmed also by Prior and Hey [21], who give the MgO:FeO ratios for the silicate part of the stony meteorites based on about 150 analyses. These data, in percent, are distributed as follows:

MgO:FeO	0.5-1	1-2	2-3	3-4	4-5	5-6	6-7	over 7
%	2	6	29	36	15	3	3	4

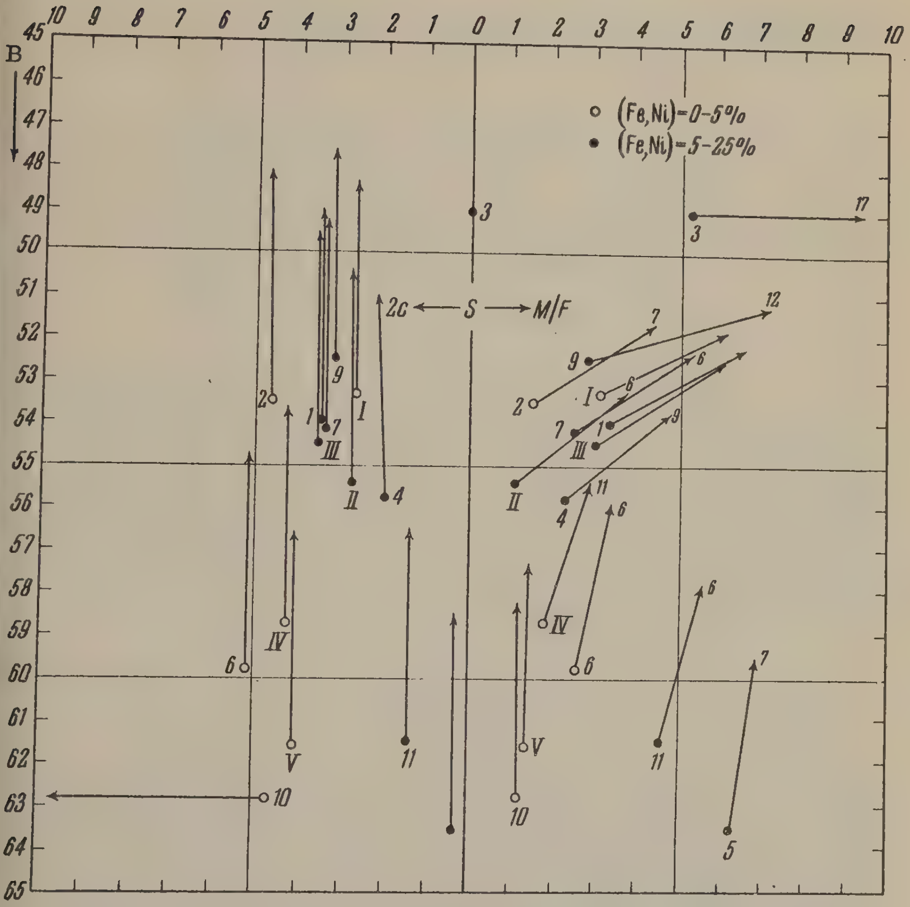

Fig. 19. Chemical Composition Diagram of Stony Feldspar-free meteorites of the USSR

i.e., the MgO:FeO ratio is between 1 and 4 in over 70% of all analyzed meteorites, most of which contain meteoric iron. Such meteorites evidently represent the zone of "oxygen deficiency", i.e., the deeper part of the sima--the peridotite-dunite layer or intersphere. These data suggest that beneath the sial the sima shell consists of three zones:

Zones	M/F
Ultraferbasites and ultraalbasites	4–7
Hypermagbasites	8–12
Zone with metallic iron	1–4

The second characteristic of stony meteorites revealed by Fig. 19 is the peculiar normative mineral composition of meteorites.

Analogues of	Amount
Dunite	2
Peridotite	4
Transitional between peridotite and bronzitite	8
Bronzitite	1

The composition of the predominant group of meteorites, transitional between peridotite and bronzitite, is practically unknown among terrestrial ultrabasic rocks, as can be seen from Figs. 5-17. But so far as the chrome spinels (2c) are concerned, the stony meteorites are entirely analogous to the terrestrial ultrabasic rocks. The stony meteorites are not serpentinized, which indicates the appropriateness of characteristic h for the terrestrial ultrabasic rocks. The only exception to this is the "Boriskino" meteorite (No. 10). In this meteorite, according to Zavaritskii and Kvasha, all iron was determined as iron oxide.

Summary

The data on the essential and accessory rock-forming minerals of ultrabasic rocks have been reviewed, i.e., the data on those oxides which are present in amounts of over 0.1%. These data do not exhaust the material on the petrochemistry of ultrabasic rocks. It is generally known that the ultrabasic rocks contain from 0.1 to 0.15% alkalies. The attempt to explain their presence as being due to contamination by vadose waters is not valid, for meteorites also contain alkalies. No less characteristic of the ultrabasic rocks is the presence of the oxides of titanium, nickel, manganese, cobalt and others. Finally, elements present in traces, those of the platinum group elements and scandium, copper and others, also are characteristic of ultrabasic rocks. The petrochemistry of rare and dispersed elements in ultrabasic rocks has been studied very little as yet; it must be investigated in the near future.

REFERENCES

1. Sobolev, N.D. Ul'trabazity Bol'shogo Kavkaza (Ultrabasic rocks of the Greater Caucasus). Gosgeolizdat, Moscow, (1952).
2. Zavaritskii, A.N. Izverzhennye Gornye Porody (Igneous rocks). Izd. Akad. Nauk SSSR, Moscow, (1955).
3. Barth, T. Teoreticheskaya Petrologiya (Theoretical petrology). Izd. inostr. lit., Moscow, (1956).

4. Sobolev, N. D. Ul'traosnovnye Porody i Svyazannye s nimi Poleznye Iskopaemye. V kn. Issledovanie Mineral'nogo Sostava Syr'ya (Ultrabasic rocks and associated ore deposits. In the book: Investigation of mineral composition of raw materials). Gosgeoltekhizdat, (1955).
5. Nemova, Z. N. Sbornik Analizov Russkikh Izverzhennykh i Metamorficheskikh Gornykh Porod (Collection of analyses of Russian igneous and metamorphic rocks). Tr. geol. kom. No. 186 (1930).
6. Struve, E. A. Sbornik Analizov Izverzhennykh i Metamorficheskikh Porod SSSR (Collection of analyses of igneous and metamorphic rocks of the USSR). Institut geol. nauk AN SSSR. Petrografiya SSSR, ser. II, No. 5, (1940).
7. Zavaritskii, A. N. Pereschet Khimicheskikh Analizov Izverzhennykh Gornykh Porod (Recalculation of chemical analyses of igneous rocks). Izd. Akad. Nauk SSSR, Moscow (1941).
8. Zavaritskii, A. N. Vvedenie v Petrokhimiyu Izverzhennykh Gornykh Porod (Introduction to the petrochemistry of igneous rocks) Izd. Akad. Nauk SSSR, Moscow, (1950).
9. Paffengol'ts, K. N. Sostoyanie Petrograficheskoi Izuchennosti SSSR i Zadachi Petrografii v Svete Trebovanii Geologicheskoi Sluzhby. V kn. Magmatism i Svyaz' s Nim Poleznykh Iskopaemykh (The state of petrographic knowledge of the USSR and the problems of petrography in connection with the requirements of the Geological Service. In the book: Magmatism and related ore deposits) Izd. Akad. Nauk SSSR, Moscow, (1955).
10. Pinus, G. V. Ob Osobennostyakh Sostava Ul'traosnovnykh Porod Slagayushchikh Giperbasitovye Poyasa Skladchatykh Oblastei (The peculiarities of composition of ultrabasic rocks in the hyperbasite belts of folded regions). Izvestiya Akad. Nauk SSSR, ser. geol., No. 3, (1957).
11. Tatarinov, P. M. Vostochnaya Polosa Gabbro-Peridotitovykh Intruzii Srednego Urala. Petrografiya Urala, ch. II (The eastern belt of gabbro-peridotite intrusions of the Middle Urals. Petrography of the Urals, pt. II). Izd. Akad. Nauk SSSR, (1940).
12. Padalka, G. L. Zapadnaya Polosa Porod Gabbro-Peridotitovoy Formatsii Urala. Petrografiya Urala, ch. I (The western belt of gabbro-peridotite rocks of the Urals. Petrography of the Urals, pt. I). Izd. Akad. Nauk SSSR, (1937).
13. Sergievskii, V. M. V kn. Geologicheskoe Stroenie SSSR, ch. II - Magmatizm (In the book: Geological structure of the USSR, pt. II - Magmatism), Gosgeoltekhizdat, Ural, (1958).
14. Sobolev, N. D. Materialy dlya Petrografii Tunkinskikh i Kitoiskikh Al'p (Contributions to petrography of the Tunkinski and Kitoiski alps). Soviet po izucheniyu proizvoditel'nykh sil, Akad. Nauk SSSR, (1940).
15. Pinus, G. V., V. A. Kuznetsov and I. M. Volokhov. Giperbasity Altae-Sayanskou Skladchatoi Oblasti. (Hyperbasites of the Altai-Sayan folded region). Izd. Akad. Nauk SSSR, (1958).
16. Yudin, M. I. Izvestiya Akad. Nauk SSSR, ser. geol., No. 2, (1959).
17. Mikhailov, N. P. Izvestiya Akad. Nauk KazSSR, ser. geol., No. 22, (1956).
18. Loewinson-Lessing, F. Yu. Chto Takoe Dunit? (What is dunite?) Izbr. tr. t. 1, Izd. Akad. Nauk SSSR, (1949).

19. Zavaritskii, A. N. and L. G. Kvasha. Meteority SSSR (Meteorites of the USSR). Izd. Akad. Nauk SSSR, (1949).
20. Vinogradov, A. P. Geokhimiya, No. 1, (1956).
21. Prior, G. T. and Max H. Hey Catalogue of meteorites, with special reference to those represented in the collection of the British Museum (Natural History), ed. 2, 432 pp., British Mus., London. Second edition, revised and enlarged (by Hey). (1953).

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WALL ROCK ALTERATION OF QUARTZ-PORPHYRY RELATED TO RARE-METAL MINERALIZATION

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(ABSTRACT)

The wall rock alteration of quartz porphyries accompanying rare metal ore formation is characterized by the addition of a great amount of alkali into the rock, both as potassium and as sodium. This alteration is directly related to the process of ore deposition and, apparently, synchronous with it. The scale of hydrothermal rock alteration increases strongly with depth.

The Aktash mineralized area lies in the southwestern foothills of the T'ien Shan and is localized in the marginal part of a large quartz porphyry intrusion. The latter cuts through effusive rocks: felsites, rhyolitic tuffs and ignimbrites referred to the Upper Paleozoic.

One of the characteristic features of the mineralized area is the presence of numerous faults striking northwest and northeast.

The northwest faults are older and longer than the northeast faults and are usually barren. Among the northeast faults there is one large fault which enters the mineralized area from the southwest and in the zone of contact between the quartz porphyry and the enclosing rocks branches into a number of smaller faults striking northeast.

The mineralization is usually localized in the north-south fissures connecting these ramifying faults.

Usually the ore-bearing veins fill individual fissures or series of adjacent steeply dipping fissures which are persistent in depth.

The principal minerals in the veins are calcite, molybdenite and sericite, sometimes accompanied by small amounts of quartz, chlorite, fluorite, pitchblende and pyrite.

Table 1

Results of Chemical and Spectral Analyses

No. of sample	Distance from vein, m	Oxides																Sp. G.	Cont. /kg per 1m^3 of rock	
		K_2O		Na_2O		Al_2O_3		SiO_2		MgO		CaO		FeO		Fe_2O_3			K_2O	Na_2O
		wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.	wt. %	mol. amt.			
For the upper part of the section																				
1	0,00	1,72	18	8,82	142	17,5	172	63,4	1056	0,17	5	1,19	21	1,52	21	5,17	32	2,791	48	264
2	0,50	3,89	41	3,60	58	14,1	138	70,8	1179	0,15	4	1,50	27	1,22	17	4,43	28	2,582	100	93
3	5,00	4,51	48	3,63	59	13,8	135	64,5	1074	0,24	6	0,70	13	1,36	18	3,07	19	2,525	114	92
For the middle part of the section																				
4	0,00	2,03	21	0,64	10	15,31	150	63,5	1057	1,43	35	1,45	26	n. d.		n. d.		2,482	50	16
5	0,02	1,48	16	0,77	12	14,2	139	57,6	959	0,60	15	1,23	21	1,58	22	2,74	17	2,482	37	19
6	0,05	1,45	15	3,28	53	13,05	127	63,2	1052	0,27	7	1,28	23	0,65	8	1,36	8	2,532	37	83
7	0,20	1,21	13	5,37	87	15,40	151	69,1	1150	0,23	6	1,90	34	0,57	8	0,96	12	2,532	31	135
8	0,60	1,37	15	6,32	102	13,5	132	67,4	1122	0,26	6	3,71	66	0,65	9	0,73	11	2,583	35	163
9	1,50	1,24	13	4,93	79	14,1	138	69,2	1152	0,25	6	4,17	73	0,50	7	0,64	10	2,549	31	125
10	7,00	2,74	29	3,34	54	15,2	149	70,1	1167	0,24	6	1,53	27	0,53	7	0,60	10	2,514	69	84
For the lower part of the section																				
11	0,00	3,51	37	0,00	0	15,2	149	74,0	1232	0,72	17	0,32	5	n. d.		n. d.		2,566	90	0,0
12	0,30	3,38	36	0,00	0	13,3	130	74,0	1232	0,72	17	0,40	7	3,97	54	0,99	12	2,566	85	0,0
13	2,00	4,13	44	1,02	16	15,6	152	71,5	1190	0,96	22	1,21	21	2,36	32	0,60	10	2,522	104	26
14	6,00	5,8	62	1,74	27	15,8	155	69,2	1152	0,69	17	0,92	16	1,74	24	0,07	0	2,479	144	43
15	16,00	1,05	11	5,25	84													2,545	27	134
16	26,00	2,62	28	3,20	52	15,0	147	69,0	1149	0,63	15	1,32	23	2,37	32	0,32	2	2,534	66	81

Note: n. d. represents not determined.
Comma represents decimal point.

It has been established that all veins, without exception, even the weakly mineralized ones, are accompanied by intensive alteration of the wall rock.

A partial description of this alteration, limited to the structure of the inner zones of the metasomatic aureole, is given in the paper by V. I. Rekharskii [2]. The structure of the entire hydrothermal alteration halo, from the relatively unaltered rocks to the ore bodies (especially near the lower parts of the veins where the alteration halo in quartz porphyry measures tens of meters), has not been described.

In the present paper we attempt to fill in this gap and to characterize the near-vein halos of hydrothermal alteration throughout their entire width.

Fortunately deep dissection enabled us to study the ore-bearing veins at different horizons from the level of the watershed to that of the valley floor (a vertical interval of 150-200 m). To determine the character of the near-vein hydrothermal alteration of the enclosing rocks, caused by the mineralization, we collected rock samples at different levels along traverses normal to the strike of the veins.

In addition to a detailed mineralogical and petrographical analysis, the samples were analyzed chemically for their major components. The analyses* show that in the near-vein hydrothermal alteration of quartz porphyry the alkali metal content in the rock undergoes the most substantial change. The contents of the other components change slightly (Table 1).

The analytical data were used to construct a graph for each traverse showing the distribution of the alkalies in the wall rock resulting from near-vein hydrothermal alteration due to mineralization. Only three most typical graphs are given here, which show quite clearly the behavior of the alkalies in the vicinity of the upper, middle and lower parts of the veins.

The alteration halos around the veins have a distinctly symmetrical structure. There is a considerable difference in the width of the halos around the lower, middle and upper parts of the veins.

Beginning with the lower parts of the veins, the hydrothermal alteration of the enclosing rocks presents the following pattern.

The unaltered quartz porphyry is light gray. Under the microscope it shows phenocrysts of quartz, potash feldspar (orthoclase), plagioclase (oligoclase, An_{25-26}) and rarely biotite and hornblende. Among the accessory minerals are apatite, zircon, leucoxene, fluorite, magnetite and allanite.

The groundmass of the rock consists of quartz and feldspars. Fresh rock is found only at a distance from the mineralization. No unaltered quartz porphyry has been found within the mineralized area. Here the entire rock mass has undergone weak alteration with later superimposition of intensive near-vein metasomatism. The weak areal alteration is manifested in partial chloritization of the dark minerals, slight kaolinization of the orthoclase and sericitization of the plagioclase. The sericite developed on plagioclase is an aggregate of very thin scales with interference colors of the first order, ranging from grayish-white to yellow. This, the first generation of sericite, is often accompanied by minute segregations of carbonate and quartz. The groundmass is not altered. In the slightly altered rock the content of K_2O is 2.62% and of Na_2O, 3.20%.

As the vein is approached, the plagioclase becomes strongly replaced by an aggregate of the fine scales of first generation sericite. The orthoclase phenocrysts become brown. Within 22-23 m from the vein the primary plagioclase disappears entirely (Fig. 1B), being completely replaced by first generation sericite, and orthoclase shows replacement by secondary checkerboard albite. Still closer to the vein, the amount of albite increases gradually, and at 16 m from the mineralized zone reaches a maximum, so that some of the orthoclase phenocrysts are completely albitized (Fig. 2). Together with albite, a fine-grained aggregate of quartz and carbonate develops at the expense of orthoclase. The groundmass also becomes replaced with fine-grained quartz and minute albite grains.

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*Analyses were made by Yu. P. Trusov.

Here the K_2O content decreases to 1.05% and the Na_2O content increases to 5.25%.

With closer approach to the vein, the amount of albite in the rock gradually diminishes and, together with the still unreplaced potash feldspar, is replaced with a fine-grained aggregate of quartz and carbonate. Approximately within 5-6 m of the ore zone the second generation of sericite begins to appear, replacing the secondary checkerboard albite, the potash feldspar and even the first generation sericite. The second generation sericite occurs in radiated aggregates of large scales. The size of the individual scales is up to 0.5 - 1.0 mm (Fig. 3). The color of the second generation sericite is pale green and shows very weak pleochroism and clear, bright interference colors up to the higher colors of the second order. The amoun of second generation sericite increases rapidly with approach to the vein, and within 5-6 m from it sericite becomes the predominant mineral in the hydrothermally altered rock. The K_2O content here increases to 5.8% and the Na_2O content decreases to 1.7%. Near the ore zone there is an intensiv development of fine-grained secondary quartz in addition to sericite. At the contact with the vein the country rock is a sericite-quartz mass without any trace of the primary structure (Fig. 3).

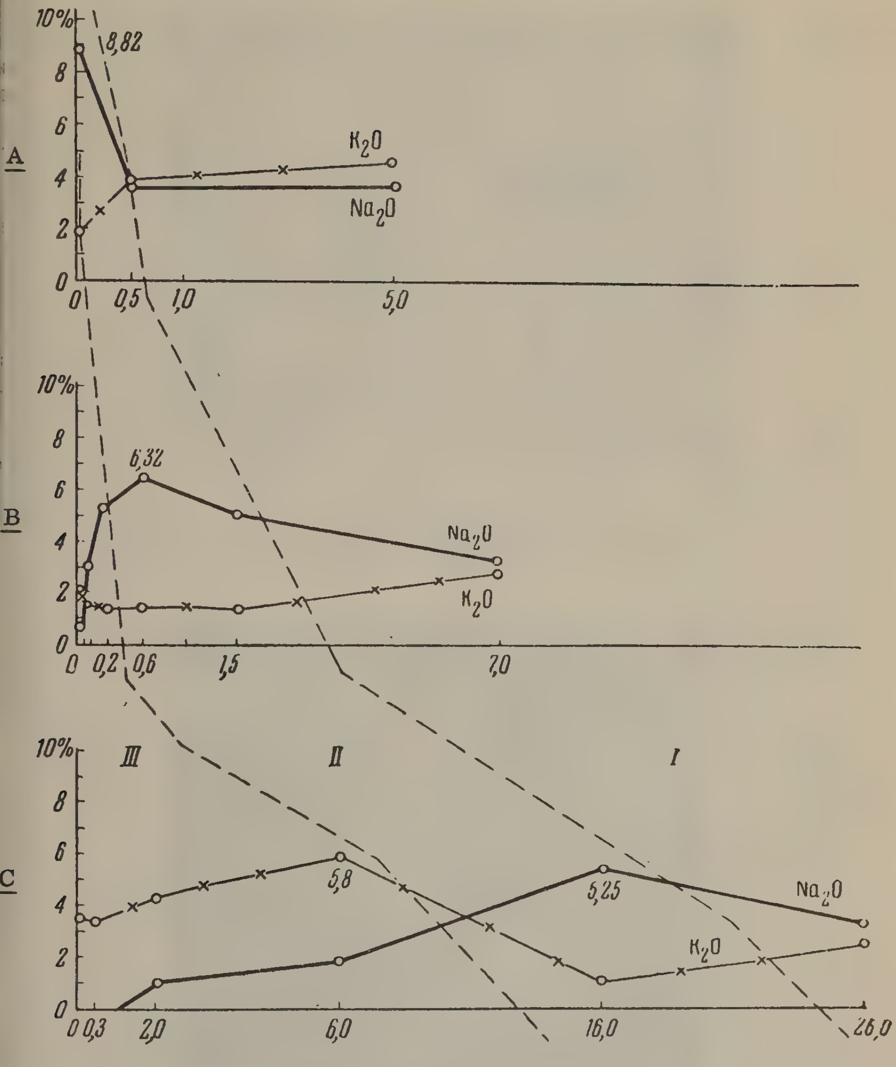
The chemical composition of the rock changes accordingly. At 1.5 m from the vein Na_2O is completely absent. The amount of K_2O decreases slightly (Fig. 1B and Table 1), due to increase in the content of quartz accompanying sericite and the complete disappearance of potash feldspar.

In the immediate vicinity of the vein, all phenocrysts (except quartz) are replaced not only by second generation sericite and fine-grained quartz but also by ore minerals, molybdenite, pitchblende and pyrite. The ore minerals usually replace the central areas of the phenocrysts, while quartz and second generation sericite develop along their peripheries. Not infrequently, however, the two suites of secondary minerals are intimately intergrown.

Very minute flakes of hematite are associated with sericite, quartz, molybdenite and pitchblende. Their presence becomes noticeable as far as 10 m from the ore zone by the dark brown or, more frequently, red-brown color which they impart to the rocks.

The association of molybdenite, second generation sericite and quartz i the rock, the replacement of the phenocrysts by these minerala and their presence in the ore-bearing veins indicate convincingly that the formation of second generation sericite and fine-grained quartz in the rock occurred synchronously with the deposition of ore minerals in the veins.

On the level of the middle parts of the veins, alteration of the country rock is similar to that already described. But the width of the halo is much less. The slightly altered rock is found within 12-15 m from the vein. The replacement of plagioclases by first generation sericite is less intensive, and sometimes even within 5-6 m of the vein relicts of incompletely sericitized plagioclase are found.



Distance from vein in meters

Fig. 1. A, B, C. Graphs showing behavior of alkalies in near-vein alteration of quartz porphyry for the upper, middle and lower parts of the ore-bearing veins

Zones of near-vein alteration
I - outer, II - middle, III - inner

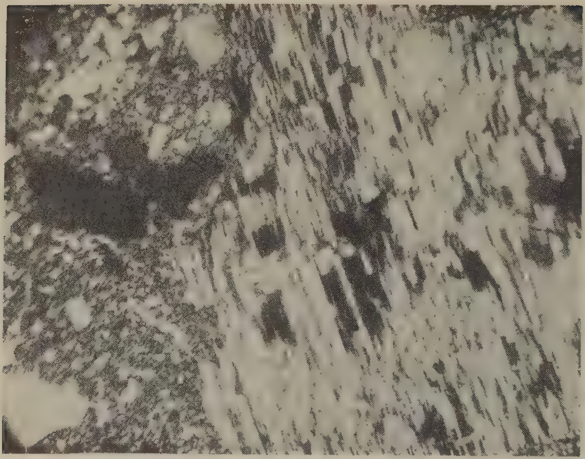


Fig. 2. Albite replacing a feldspar phenocryst. Crossed nicols (x73)

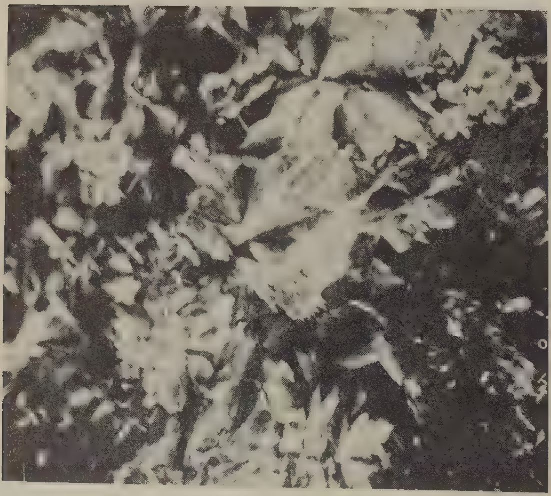


Fig. 3. Quartz-sericite aggregate near mineralized zone. Second generation sericite. Crossed nicols (x146)

However, albitization of the rock is more intensive here, its maximum eing not 16 m from the ore zone, as on the level of the lower parts of eins, but in the interval between 4-5 and 0.8-0.6 m.

The amount of Na_2O in the rock corresponding to maximum albitization s 6.32%, and that of K_2O is only 1.2% (Fig. 1B).

Second generation sericite appears only within 50-60 cm from the vein elvedge and reaches a maximum at 0-5 cm from it. Accordingly, the mount of Na_2O at the contact with the vein decreases to 0.64% and the mount of K_2O increases to 2% (Fig. 1B, Table 1).

The hydrothermal alteration halo about the upper parts of veins is also imilar to that already described, but its width is still less. The albitiza- on zone does not extend beyond 0.5 - 1 m from the vein, and the maximum f albite occurs at the vein selvedge. The amount of Na_2O at the contact is to 8.8% (Fig. 1A, Table 1).

Second generation sericite appears at 20-25 cm from the vein and some- mes withon only 1 to 2 cm from it.

In the immediate vicinity of the vein, feldspar phenocrysts are replaced molbydenite, pitchblende and second generation sericite. Often pitch- ende, pyrite and molybdenite within 1-2 cm from the contact impregnate e rock to such an extent that it appears dark-gray. The reddening of the ountry rock does not extend more than 1 m from the vein.

These data show that three well defined zones may be distinguished in e near-vein halos developed in the country rock of the Aktash mineralized rea.

In the first zone, the farthest removed from the veins, hydrothermal teration of the enclosing quartz porphyry is manifested in the chloritiza- on of the dark minerals, sericitization (first generation sericite) of agioclase and kaolinization of the potash feldspar.

The second zone of hydrothermal alteration lies nearer to the veins and characterized by intensive albitization of the quartz porphyry. Checker- ard albite develops after the feldspar phenocrysts and sometimes replaces e groundmass of the rock. The albitized zone is much narrower than the st zone. Its width increases with depth, as can be clearly seen by com- ring the traverses of the near-vein alteration halo at the levels of the wer, middle and upper parts of the vein (Fig. 1A, B, C). While the aximum albitization in the lower part occurs at 16 m from the vein, in e middle part it is from 4-5 m to 0.6 m from the vein, and in the upper rt it is very near the contact between the vein and the country rock.

The third zone of alteration is directly at the contact between the rock d the vein and is characterized by the development in the quartz porphyry large amounts of second generation sericite replacing the albitized rock d by separation of fine-grained quartz, dusty hematite, molybdenite and chblende, which, together with pyrite, quartz and second generation ricite, replace the feldspar phenocrysts. The width of this zone, like at of the albite zone, increases rapidly with depth.

These observations indicate that in our locality there is a sharply de- loped horizontal zonation in the structure of the alteration halo. The dth of the whole halo increases with depth, and so does the width of the ividual zones, indicating that the intensity of replacement of the enclos- rock increases with depth. But in both the upper and the lower parts of veins the metasomatic zones of near-vein hydrothermal alteration of rtz porphyry are the same.

On the basis of the chemical analyses and the determination of the spe- c gravity of the rock, the balance of K_2O and Na_2O in the alteration zones

Table 2

Section	K_2O, kg		Na_2O, kg	
	added	removed	added	removed
Upper part of mineralized zone	-	37.00	46.38	-
Middle part of mineralized zone	-	147.06	201.65	-
Lower part of mineralized zone	262.87	-	5.95	-

has been calculated for the lower, middle and upper parts of the vein. The results of calculation (Tables 1, 2) show that in the process of near-vein alteration considerable amounts of the alkalies were introduced into the country rock. Bearing in mind the symmetrical structure of the alteration halos, it may be said that the rock received about 538 kg of alkalies per square meter of the plane of the ore-bearing fissure. For the middle and upper parts of the veins the amount of added alkalies is somewhat less. In the middle part of the veins each square meter of the plane of the ore-bearing fissure delivered about 109 kg of alkalies to the country rock and in the upper part, about 19 kg. The maximum addition of Na_2O into the rock coincided with the maximum development of albite in the zone of albitization and the maximum addition of K_2O, with the maximum development of the second generation sericite.

Thus, even the results of an approximate calculation show that the ore-bearing solutions brought and deposited large amounts of alkalies in the country rock. In the lower parts of the veins the reaction between them and the enclosing rock was more intensive, as indicated by the greater width of the hydrothermal alteration halos and by the amount of introduced substances (Tables 1 and 2).

The presence in the near-vein halos of secondary potassium and sodium aluminosilicates indicates that the ore-bearing solutions contained both potassium and sodium ions but the first was fixed in the rock in much large amounts at depth and the second in the upper parts of the veins.

Summary

1. The characteristic feature of the near-vein hydrothermal alteration of quartz porphyry is the considerable addition to the enclosing rock of the alkalies — potassium, mainly in the lower parts of the veins, and sodium in its middle and upper parts.

2. A horizontal zoning has been detected in the alteration halo and three hydrothermal zones have been distinguished.

The first zone, the farthest from the veins, is characterized by the development of chlorite and first generation sericite replacing the phenocrysts.

The second zone is characterized by the predominant development of albite.

The third zone, directly at the contact with the veins, is characterized by the formation of second generation sericite and quartz together with subordinate amounts of molybdenite, pyrite, pitchblende and finely dispersed oxides of iron.

3. The width of the near-vein hydrothermal alteration halos in the enclosing rock increases rapidly with depth.

REFERENCES

1. Vainshtein, E. E. and V. V. Korolev. Zh. analit. khimii, 11, 5, 627 (1956).
2. Rekharskii, V. I. Geokhimiya, No. 3 (1957).

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RETENTION OF ARGON IN MICAS*

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(ABSTRACT)

The article gives the results of studying the preservation stage of argon in hydrated biotites as well as of the mode of extracting argon from them at different temperatures. It has been established that the hydration of biotite does not influence the preservation state of argon in it under natural conditions. At the same time, being heated, the hydrated argon isolates (loses) the chief mass of argon at considerably lower temperature than the non-hydrated biotite, and the higher the hydration degree, the greater this loss.

The wide application of the K/Ar method of age determination is made possible by the remarkable ability of potassium-bearing minerals to retain their radiogenic argon. Micas show the best argon retention, and they are often taken as standards with which argon retention in other potassium minerals is compared. But micas, as any other mineral, are subject to various alteration processes which may disturb their K^{40}-A^{40} ratio. An understanding of the effect of these processes on argon retention and thus on the results of absolute age determination is essential.

Hydration is the most common process of mica alteration. It may go on under hypogene conditions by the action of hydrothermal solutions (usually soon after the crystallization of the mica, that is before any argon has accumulated) or in the zone of weathering. In reference to the former process we present the results of the study of hypogene hydrothermal hydration

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of mica in the Buldym deposit and its effect on argon retention.

The Buldym vermiculite deposit is in the central Urals near the north end of the Vishnevoe mountains near Lake Buldym. According to Ozerov [3] the deposit is related to a mass of serpentine lying in the midst of granite gneisses. The serpentine is largely altered into talc-carbonate rock. In the east, nepheline syenites (miaskites) of the Vishnevoe mountains are in immediate contact with serpentinite. Biotite largely altered to vermiculite lies in the middle of the talc-carbonates in a large lens about 135 meters long and up to 20 meters thick, striking northeast. A zone of actinolite or tremolite lies between the biotite and the enclosing rocks.

Vermiculite makes up the whole lens in places, but in some parts we find imerinite (a soda amphibole), zircon and magnetite.

The origin of the deposit is evidently connected with the late magmatic intrusion of nepheline syenites. The biotite and amphiboles were formed by the intrusion of ultrabasic rocks along fractures which served to facilitate upward motion of hot fluids. A little later, in the hydrothermal stage, biotite hydrated to vermiculite and the surrounding rocks changed to talc-carbonate.

The primary mica in the deposit is a magnesium biotite. Its hydration resulted in a series of hydromicas with various degrees of water saturation. The deposit does not contain vermiculite in the strict meaning of the word - i. e. hydromica with no potassium and with 20% or more of water - but the physical properties of the Buldym hydromicas are very close to vermiculite and the micas are a good industrial vermiculite material.

Five samples representing different degrees of hydration of the biotite were taken for study. Their crystal formulae and properties are given in Table 1. Complete chemical analyses of the samples were made by L. I. Metikh and X-ray analysis by B. A. Yunikov [2].

As seen from Table 1, the samples were hydrated to a different degree and differed from one another chemically and physically. The content of potassium gradually decreases with hydration as the potassium is replaced by the oxonium [H_3O^+] cation. In the most highly hydrated sample, No. 5, the potassium content, compared to sample 1, is lower by a factor of two, with a corresponding increase in water content by more than a factor of four. In addition to the potassium replacement by oxonium, the hydration also brings about the displacement of fluorine by the hydroxyl cation and the appearance of molecular water. In sample 5 the amount reaches three molecules of water to four of biotite.

Together with hydration, the ferrous iron is oxidized. In sample 5 the amount is lowered almost by a factor of eight, compared to sample 2. Magnesium increases with hydration. In other words, hydration is accompanied by broad changes in composition. These changes are accompanied by a change in physical characteristics: lowering of the refractive index, loss of elasticity, browning and gradual acquisition of the industrially valuable characteristics of vermiculite, i. e. great expansion by heat in the direction of the c axis.

Gruner [5] and B. A. Yunikov [2] have shown by X-ray analysis that the structure of mica changes sharply with hydration. Mixed layer structures are formed, consisting of interlayered "sheets" of biotite, hydrobiotite and vermiculite.

These profound changes in the structure of biotite are of interest in the study of argon and its retention in micas of various degrees of hydration.

Argon content in the mica samples was determined volumetrically with an apparatus based on the design of V. G. Khlopin and E. K. Gerling.

Table 1

Composition and Properties of Buldym Micas

Sample No.	Crystal Formula	Index α	Color and Elasticity	Change when heated to 850° C
1	$(\mathrm{K}_{0.91}\mathrm{Na}_{0.04}\mathrm{H}_3\mathrm{O}_{0.05})_{1.0}(\mathrm{Mg}_{2.35}\mathrm{Fe}^{2+}_{0.43}\mathrm{Fe}^{3+}_{0.18}\mathrm{Mn}_{0.02})_{2.98}$ $/(\mathrm{Si}_{2.83}\mathrm{Ti}_{0.04}\mathrm{Al}_{1.14})_{4.01}\mathrm{O}_{10}/\cdot(\mathrm{OH}_{1.18}\mathrm{F}_{0.82})_{2.0}$	1.591	Dark green, elastic flakes (like normal biotite)	Barely noticeable decomposition of flakes and books
2	$(\mathrm{K}_{0.87}\mathrm{Na}_{0.08}\mathrm{H}_3\mathrm{O}_{0.05})_{1.0}(\mathrm{Mg}_{2.10}\mathrm{Fe}^{2+}_{0.62}\mathrm{Fe}^{3+}_{0.16}\mathrm{Mn}_{0.01})_{2.89}$ $/(\mathrm{Si}_{2.77}\mathrm{Ti}_{0.09}\mathrm{Al}_{1.20})_{4.06}\mathrm{O}_{10}/\cdot(\mathrm{OH}_{1.53}\mathrm{F}_{0.42})_{1.95}$	1.591	same	Slight but clear decomposition of flakes; lightens
3	$(\mathrm{K}_{0.56}\mathrm{Na}_{0.07}\mathrm{H}_3\mathrm{O}_{0.37})_{1.0}(\mathrm{Mg}_{2.62}\mathrm{Fe}^{2+}_{0.12}\mathrm{Fe}^{3+}_{0.36}\mathrm{Mn}_{0.02})_{3.12}$ $/(\mathrm{Si}_{2.77}\mathrm{Ti}_{0.05}\mathrm{Al}_{1.05})_{3.87}\mathrm{O}_{10}/\cdot(\mathrm{OH}_{1.43}\mathrm{F}_{0.57})_{2.0}\cdot 0.57\mathrm{H}_2\mathrm{O}$	1.570	Brownish green and bronzy. Flakes soft	Slight decomposition and swelling. Color silvery white
4	$(\mathrm{K}_{0.54}\mathrm{Na}_{0.07}\mathrm{H}_3\mathrm{O}_{0.39})_{1.0}(\mathrm{Mg}_{2.77}\mathrm{Fe}^{2+}_{0.09}\mathrm{Fe}^{3+}_{0.28}\mathrm{Mn}_{0.01})_{3.15}$ $/(\mathrm{Si}_{2.86}\mathrm{Ti}_{0.07}\mathrm{Al}_{0.96})_{3.89}\mathrm{O}_{10}/\cdot(\mathrm{OH}_{1.73}\mathrm{F}_{0.27})_{2.0}\cdot 0.53\mathrm{H}_2\mathrm{O}$	1.567	Greenish-brown with bronzy cast. Flakes soft, least elastic	same
5	$(\mathrm{K}_{0.50}\mathrm{Na}_{0.10}\mathrm{H}_3\mathrm{O}_{0.44})_{1.04}(\mathrm{Mg}_{2.81}\mathrm{Fe}^{2+}_{0.08}\mathrm{Fe}^{3+}_{0.37}\mathrm{Mn}_{0.01})_{3.27}$ $/(\mathrm{Si}_{2.86}\mathrm{Ti}_{0.03}\mathrm{Al}_{0.96})_{3.85}\mathrm{O}_{10}/\cdot(\mathrm{OH}_{1.68}\mathrm{F}_{0.32})_{2.0}\cdot 0.72\mathrm{H}_2\mathrm{O}$	1.569	same	Same, α increased to 1.588

Atmospheric contamination was monitored with an MS-2M mass spectrometer. The results are given in Table 2 and graphically in Fig. 1. It can be seen that the potassium content is directly proportional to the argon content and that the argon retention is about 100% regardless of the great changes in composition and structure. The measured absolute age of all samples is exactly the same, 304 ± 5 m.y., identical with the age obtained by the lead method for other minerals of the Ilmen-Vishnevoe Gory complex.

Table 2

Relation of argon, potassium and water content in the Buldym micas

Sample No.	Contents			$\frac{Ar^{40}}{K^{40}}$	Deviation of A^{40}/K^{40} from the mean (%)
	H_2O (%)	K (%)	Ar 10^{-8} gg		
1	3.18	8.24	18.99	0.0188	1.5
2	3.40	7.70	17.07	0.0181	2.3
3	10.08	5.08	11.33	0.0188	1.5
4	12.10	4.80	10.22	0.0181	2.3
5	13.76	4.26	9.37	0.0188	1.5
Average				0.0185	1.8

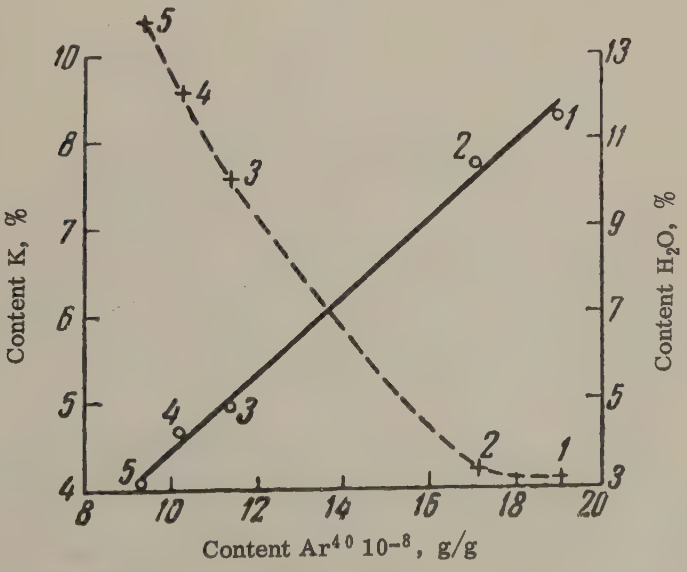

Fig. 1. Relation of argon content to potassium content (solid line) and water content (dotted line) in hydrobiotites of the Buldym deposit.

Hydration being accompanied by progressive loss of potassium, the argon and water contents are clearly related. The slight deviation from a straight-line relationship in the curve of Fig. 1, between samples 1 and 2 is caused by potassium loss out of proportion with oxonium replacement and a doubling of the sodium content (see Table 1).

These results show the surprising ability of mica to retain radiogenic argon. The regularity of the argon-potassium relationship under such conditions is possible only when the radiogenic argon atom remains in the place where it was formed and not in any other position.

The great argon retentivity, after severe hydration of the mica, is explained by the structure of the micas and the regular changes which occur as a result of hydration. Hydration produces mixed-layer structures. All changes occur layer-by-layer and profound alteration of a thin sheet does not affect the equally thin neighboring sheet. As a result, the books contain thin layers of unaltered biotite amid hydrobiotite and vermiculite layers. The hydrobiotite itself also consists of layers of biotite and vermiculite, but in statistically disordered distribution [2, 5].

The basal interlayer distances are different in the three structural forms, for they increase with increasing degree of hydration as a result of the intrusion of water molecules or hydroxyl ions into the spaces between the layers of the original phase biotite. In biotite the unit cell measures 10 Å in the c direction, in hydrobiotite 11.8 Å and in vermiculite 14.4 Å.

All mixed-layer micas, thus show a layered polymorphism and are characterized by a multilayered unit cell containing either 6 or 24 individual layers. Layers of various types may together compose nearly stable structures as well as structures built-up of only one type of layer.

This structure of biotite and all its hydrated varieties favors the retention of argon in them. The layer-by-layer alteration assures undisturbed conditions in those layers in which potassium is preserved and this leads to preservation of the K/Ar ratio as in unaltered biotite.

However, argon would be preserved in these structures only if it had no chance to migrate from the place of its origin. Inasmuch as argon is completely preserved, we conclude that it occupies only the places of its parent potassium and that its atoms are strongly deformed [sic].

Water in hydromicas occurs in three positions: as molecular water, as the hydroxyl ion and in the form of oxonium (see Table 1). Different quantities of these three forms of water, each bound with different energy in the mineral, presumably determine the behavior of the mica during dehydration by heating. To study the mechanism of dehydration and argon behavior we heated the samples. N. V. Bakhareva dynamically weighed the samples by means of a torsion balance while they were heated in air. All showed weight loss almost exactly corresponding to their total water content, although this loss was partly offset by oxidation of ferrous iron in the less hydrated samples (Nos. 1 and 2). This oxidation occurs at temperatures of 350-500 and 850-900° C.

Fig. 2 shows the curves of weight loss in two extreme samples: No. 1 - almost unaltered biotite - and No. 5 - highly hydrated biotite with 14% water. The same graph also includes curves of argon loss produced by heating these same samples.

To study the argon loss, a sheared mica sample was sealed in a quartz tube and heated to the desired temperature for 10-12 hours to assure full argon release. The separated gas was captured on charcoal at liquid-nitrogen temperature and then cleaned with metallic calcium.

The volume of the argon was measured on a McLeod gauge and air contamination by the MS-2M mass spectrometer.

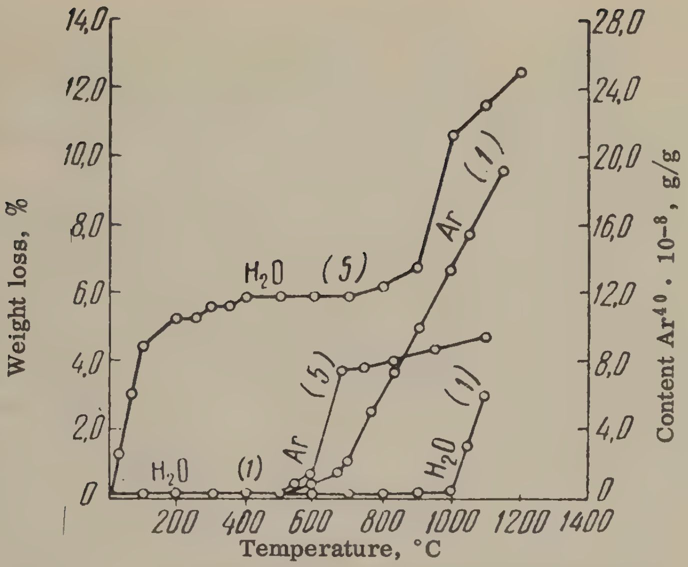

Fig. 2. Argon and water release on heating (sample No. 1) and hydrobiotite (sample No. 5) of the Buldym deposit.

The released argon was first measured one hour after the desired temperature was reached. Additional argon was then measured every 1-1/2 to 2 hours at the same temperature. The rate of argon release was entirely analogous to that observed by E. K. Gerling and I. M. Morozova [1] when they determined the activation energy of argon release from micas. Almost all argon to be released at a given temperature comes off at once when the temperature is reached and only very small amounts come off with more time at the same temperature. The results of these experiments at various temperatures are shown in Fig. 2.

The graph of argon release from sample 1 has two segments. The first, short and flat, goes up to 675° C when only little argon is liberated. The other segment, a sharply rising straight line, shows the regular release of argon in the interval 675–1100° C, as a directly proportional function of temperature. Sample 5 presents a different picture. The argon release begins at a lower temperature and can be divided into three stages. From 500–600° C about 15% of the argon is released; from 600–675° C about 65% of the total argon is released rapidly in bursts; and from 675 to 1100° C the remaining 21% of the argon are gradually released.

Although the argon release from biotite and its hydrated variety begins almost at the same temperature of about 500–550° C, the rate of release with further heating is quite different for the two forms. Hydrated mica releases the bulk of its argon at relatively low temperatures. Sample 5, for example, released 80% of its argon below 700° C, whereas sample 1 had lost only 10% of its argon at that temperature. Apart from this great difference in the kinetics of argon release, the complete removal in any case occurs only at relatively high temperatures, near 1100° C.

The low-temperature release of argon from hydromica is most probably dependent on its structure, which differs from non-hydrated mica by greater "openness", the presence in the multilayered books of vermiculite layers with larger unit cell dimensions, and the remarkable property of swelling when heated. All this greatly facilitates argon diffusion from the lattice.

It is to be expected that the rate of argon release from micas would depend on the degree of their hydration.

The dehydration of samples 1 and 5 also proceeded at different rates. Sample 1, containing only combined water, was dehydrated only in the narrow interval 1000-1100° C when the biotite structure is completely destroyed. High hydrated sample 5 loses its water in several steps. Molecular water, hygroscopic and interlayered, is released up to 400° C [4]. Further heating from 700-1200° releases combined zeolitic water and the combined water from the oxonium and hydroxyl ions. The structure is characteristically destroyed only near the top of the interval at temperatures near 1100-1200° C. At lower temperatures the structure is preserved and the atoms merely regroup with the loss of water [4].

There is no clear connection between argon and water release. In both cases argon precedes water: the bulk of it is released in a temperature interval where there is either little or no loss of water (see Fig. 2).

The complete argon retentivity of micas with different degrees of hydration shows that the different behavior of argon during the heating of the micas cannot serve as a measure of this retentivity. Hydromicas, with relatively low activation energy for argon release, as we have shown, conserve their argon just as well as non-hydrated biotite.

Summary

We have studied argon release from 5 samples of variously hydrated mica of the Buldym deposit. Our results follow:

1. The profound changes in composition, structure and properties of biotite, caused by hydrothermal alteration, show no effect on argon retentivity. Biotite and its hydrated varieties alike retain all their radiogenic argon.

2. Complete argon retention in heavily altered hydromicas is caused, on one hand by the location of the radiogenic argon atoms in the positions of the decayed parent potassium atoms.

On the other hand, the conservation of argon in hydromicas and the impossibility of its migration in the mineral are the result of the layer-by-layer replacement of potassium by oxonium and other alteration processes connected with the hydration. The mixed-layer structures of hydromicas, representing multi-layer alternation of biotite, hydrobiotite and vermiculite, leave undistrubed those layers in which the potassium is conserved.

3. Compared with biotites, hydromicas lose argon more easily when heated, due to the greater "openness" of their structure, which facilitates argon diffusion on heating. A relation between argon and water release is lacking. Argon precedes water: most of it is lost ahead of the water in a temperature interval when water losses are small or none.

4. The behavior of argon on heating under laboratory conditions cannot serve as a measure of its retentivity in micas. Hydromicas with a low activation energy for argon loss retain their argon just as well as unhydrated biotite.

REFERENCES

1. Gerling, E. K. and I. M. Morozova, Opredelenie energii aktivatsii vydeleniya argona iz slyud. Determination of the activation energy of argon release from micas. Geokhimiya, No. 4 (1957).
2. Ovchinnikov, L. N., B. A. Yunkov, and L. I. Mettikh, O sostave i stroenii gidroslyud Buldymskogo mestorozhdeniya. Composition and structure of hydromicas of the Buldym deposit, Trudy Gorno Geol. Inst. Ural. Filiala Akad. Nauk, Miner, Sb. No. 5.
3. Ozerov, K. N. V knige "Kurs nerudnykh mestorozhdenii." Mica, in the book "Course in non-metallic deposits," Part I, Deposits of mineral ray materials, O. N. T. I., (1934).
4. Tsvetkov, A. I. and E. P. Valyashikhina, Materialy po termicheskomu issledovaniya mineralov. Thermal study of minerals, III. Micas. Trudy I. G. E. M. No. 4 (1956).
5. Gruner, J. W. The structures of vermiculites and their collapse by dehydration, Amer. Mineralogist, 19, No. 12 (1934).

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FACTORS DETERMINING THE GEOCHEMICAL DISTRIBUTION OF SCANDIUM

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(ABSTRACT)

Scandium is a typical lithophylic trace element. The noticeable irregularity of its distribution in rocks and minerals is caused by its typically lithophylic properties of the relatively strong base which is able to accumulate in the pegmatite-hydrothermal stage, impoverished in magnesium and iron compounds and enriched in anions (e.g. wolframate, niobate ions) which are scandium precipitators.

Scandium does not participate in redox processes and in coals it accumulates not at the expense of reduction but of sorption.

Scandium participates more intensively in the formation of complex compounds than the rare earths which increases its migration ability.

The irregularity of the scandium distribution in silicate minerals is caused by the energy values of the crystal lattice.

There are at present sufficient quantitative data on the distribution of scandium in rocks and minerals, and it is possible to draw certain conclusions as to the causes determining its geochemical distribution.

The content of scandium in minerals and rocks has been investigaged by G. Eberhard [1], V. Crookes [2], V.I. Vernadskii [3], R.J. Meyer [4], V.M. Goldschmidt [5], W. Tongeren [6], I. Oftedal [7], A.S. Dudykina [8], L.F. Borisenko [9], G. DeVore [10] and many others.

References [1-6, 8 and 10] give data on the distribution of scandium; in references [5, 8, 10] the distribution of scandium in paragenetically related minerals is discussed; and in references [5, 7, 8 and 9] conclusions are drawn on the relationship between scandium content and genetic characteristics. Borisenko presents a genetic classification of scandium occurrences, and DeVore explains the difference in scandium content in paragenetically related minerals of similar composition by the different changes in the dimensions of the crystal lattices caused by the entry of scandium.

Although scandium is a typical dispersed mineral, its distribution among rocks and minerals is very irregular.

The cause of this irregularity is ascribable to the many factors determining the distribution of scandium.

These factors are:

1. The electronic structure of scandium ion (8-electron outer shell of the inert gas type) places it among the lithophile elements. It explains the difficulty of reducing scandium to the metallic state and shows why it does not occur in nature as a native element and is absent from the native elements (platinum, gold, silver). The nonexistence of natural scandium arsenides indicates its complete lack of siderophile properties. Scandium does not form sulfides, selenides, or tellurides and is practically absent as a trace element in these minerals. This shows that it is completely devoid of chalcophile properties. In nature scandium is concentrated entirely in oxygen compounds, mainly silicates, titano-tantalo-niobates, and phosphates. The nonexistence of natural scandium fluorides and its absence as an admixed element from fluorite and other fluorine minerals, while aluminum and the rare earths do form such minerals, is explained by the fact that it is less basic than yttrium and especially cerium, and hence scandium fluoride hydrolyzes easily under endogenic conditions. At the same time, scandium is a stronger base than aluminum and cannot, under natural conditions, form anion complexes of the cryolite type, $[AlF_6]^{3-}$.

The scandium ion is a structural analogue of yttrium and lanthanum, and this explains its frequent association with the rare earths and particularly with the yttrium earths. Conversely, thortveitite, $Sc_2Si_2O_7$, has a relatively high yttrium content. The association of scandium with yttrium is found also in spessartite, zircon, and in some sedimentary rocks enriched in organic matter.

Scandium is rather seldom associated with aluminum, although the two elements belong to the same group of the periodic table, and replaces it diadochically only when aluminum has 6-coordination in the crystal lattice (beryl, muscovite, and possibly the aluminum hydroxides in bauxite).

2. The ionic radius of scandium, 0.83 Å, according to Goldschmidt, is identical with the ionic radius of ferrous iron and is very near in size to the ionic radii of magnesium (0.78 Å), manganese (0.91 Å), and zirconium (0.87 Å). The polarization properties of these elements are very similar, and this provides scandium with broad possibilities for heterovalent diadochy; and since these elements are much more abundant, scandium appears in the lattices of their minerals as a typical dispersed element. Relatively rarely scandium occurs as an isovalent diadochic substitute for aluminum and yttrium.

Aluminum has a much smaller ionic radius (0.57 Å) than scandium (0.83 Å), and this discourages diadochy between them, for lattice energy is decreased by the replacement of a smaller ion by a larger one. As for yttrium, although its ionic radius is considerably larger (1.06 Å) than that of scandium, the diadochic replacement of yttrium by a somewhat smaller ion with the same charge is energetically "advantageous", and hence scandium occurs much more frequently in yttrium than in aluminum minerals.

The substitution of bivalent ions (magnesium, iron, manganese) by trivalent scandium is energetically advantageous only if there occurs a simultaneous compensating replacement of $SiO_4{}^{4-}$ by an equivalent amount of AlO_4^{5-}. The disadvantageous substitution of scandium for zirconium is compensated to a certain extent by the simultaneous replacement of SiO_4^{4-} by PO_4^{3-}.

3. The high valence of scandium (3) together with its relatively large ionic radius and the ionic type of its compounds are responsible for the absence of easily volatilized molecular scandium compounds. Scandium is not concentrated in nature by gaseous transfer, and this important geochemical process, so important in separating isomorphous mixtures of ionic compounds, is of no significance in the case of scandium.

4. The ionic potential of scandium (the ratio of charge to ionic radius) characterizes it as an element forming a rather strong base practically devoid of amphoteric properties (distinct from aluminum, gallium, etc.), and requiring a fairly high pH, of 6.1, for the precipitation of the hydroxides*. The strong basic properties of scandium determine its weaker hydrolysis as compared with aluminum, iron, and titanium compounds, and the absence of amphoteric properties explains why scandium is not transported by alkaline solutions in the supergene zone (although in the presence of carbonates, scandium dissolves in the form of complex carbonate compounds). The ionic potential of scandium (3.62)** is near that of thorium (3.64), yttrium (2.83), and zirconium (4.60); the pH at which scandium hydroxide is precipitated is similar to that required for the precipitation of $Be(OH_2)$ (5.7), $Fe(OH)_2$ (5.5), $Ni(OH)_2$ (6.7), $Co(OH)_2$ (6.6), and is quite different from that required to precipitate $Al(OH)_3$ (4.1), $Fe(OH)_3$ (2.48), $Th(OH)_4$ (3.5), and $Zr(OH)_4$ (2.05 - 2.47).

These properties of scandium, together with the low solubility of its hydroxide, $1.4 \cdot 10^{-7}$ mole/l, and the considerable adsorbability of scandium, are responsible for its negligible content in ocean water ($4 \cdot 10^{-9}$%), which is 150,000 less than its content in the lithosphere; i.e., only about 0.001% of scandium delivered from the lithosphere with the products of weathering is retained in the water, the bulk of it going into the sedimentary rocks.

5. The occurrence of scandium in natural compounds in the trivalent state only indicates that it does not participate in the oxidation-reduction processes in the earth's crust and therefore, in the related processes of concentration and dispersion of the elements. The potential required to reduce trivalent scandium to the bivalent state (E_h = 1.498 v), measured in 1937 by Noddack and Holleck [11], far exceeds the reduction potentials of the reactions occurring in the earth's crust, and because of the oxidizing action of the ever present water, natural bivalent scandium compounds are nonexistent, just like bivalent chromium and vanadium compounds (E_h = 0.41 and 0.20 v, respectively). As for the relatively high scandium concentrations in some coals, they must be due entirely to the sorption processes or to the formation of difficultly soluble complex between scandium and the organic compounds of the coal beds.

6. Scandium forms stable sparingly soluble compounds, and in this form is to some extent separated and concentrated by both hypogene and supergene processes. The chemical composition of these compounds is not the same in the two types of processes: under hypogene conditions scandium oxide forms compounds with WO_3 (in wolframite), Nb_2O_5 (in khlopinite),

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*Hydrolysis of scandium from acetate solutions gives pH = 4.9.

**More precisely the ratio of valence to ionic radius.

TiO_2 (in brannerite), SiO_2 (in thortveitite and as a trace in many silicates), while under supergene conditions it unites with PO_4^{3-} and some varieties of organic matter (accumulation of scandium in certain types of coal).

7. According to K. B. Yatsimirskii and V. P. Vasil'ev [12], scandium has a stronger tendency to form complex compounds, particularly with fluorine, than the yttrium and especially cerium earths (dissociation constant of $ScF_6^{3-} = 5 \cdot 10^{-18}$), but weaker than aluminum (dissociation constant of $AlF_6^{3-} = 1.44 \cdot 10^{-20}$). The carbonate scandium complexes $[Sc(CO_3)_2]^{1-}$ and $[Sc(CO_3)_4]^{5-}$ described by Sterba [13] are more stable than the analogous rare earth complexes.

The dissociation constants of the hydroxide complexes are: $2.0 \cdot 10^{-15}$ for $CeOH^{2+}$, 5.10^{-13} for $ScOH^{2+}$, and $1.38 \cdot 10^{-9}$ for $AlOH^{2+}$. The compounds of scandium with soil acids have not been studied. The last three types of complexes are characteristic of the supergene zone, but transfer in the form of fluorine complexes (and in part carbonate complexes) may occur during the endogenetic processes.

The fact that the elements may migrate not only as such but also in the form of complex compounds considerably broadens the possibilities of their migration, and therefore of their concentration.

8. The selective sorption of scandium compounds has not been studied, and we may judge of it only from geochemical facts. These are the adsorption of scandium on coal and some phosphorites and limonites. Having a rather large ionic radius, scandium does not tend to form colloids, but its relatively high valence favors its adsorption.

9. The difference in the amount of free energy released by the entry of scandium into different silicate lattices results in its very unequal distribution among paragenetically related and chemically similar silicates. Thus, in the paragenesis hornblende-biotite-almandine, the last contains the most scandium, hornblende less, and biotite the least. In the magnesium-iron orthopyroxenes, there is always more scandium than in the associated olivine, although this mineral contains the same elements.

The behavior of scandium during geochemical processes varies, depending on the composition of the magma. In basic rocks scandium is largely fixed during the magmatic stage by dispersion through the ferromagnesian aluminosilicates, and gabbros, pyroxenites, and hornblendites are richer in scandium than peridotites and dunites. Borisenko notes that basic dike rocks are enriched in scandium as compared with the parent rocks. In granitic rocks scandium is concentrated during the pegmatitic stage and especially in the greisen formed during the pneumatolytic-hydrothermal stage. The enrichment in silica and volatiles (water, in part) favors the accumulation of scandium, while the absence from the system at this time, of most iron and magnesium, the elements in whose minerals scandium tends to disperse, favors relatively high concentrations of scandium in cassiterite, wolframite, beryl, muscovite, spessartite and, to some extent, in schorlite.

This is the time of the main separation of scandium; the later, lower temperature hydrothermal deposits are poor in it.

In skarns and similar metasomatic rocks, scandium concentrations, except for one unusual example, are unknown. Alkalic rocks, agpaitic nepheline syenites, do not favor the accumulation of scandium. This is due to the low solubility of scandium, a relatively strong base (but not an alkali element), in an alkaline medium (scandium has no amphoteric properties) low in silica. Large amounts of silica are evidently required for the transport and accumulation of scandiu.

In sedimentary rocks, scandium is accumulated in clays, particularly ferruginous clays, in some bauxites and, to a somewhat greater degree, in sedimentary phosphorites, especially those enriched in organic matter, and in some coals.

Concentrations of scandium in sandstones and limestones are relatively low, it is usually absent from manganese ores, and it does not occur in gypsites and rock salt deposits.

These are the factors determining the geochemical distribution distribution of scandium and reflected in its geochemical history.

REFERENCES

1. Eberhard, G., Sitzungsberichte Königl. Preuss. Akad. Wissensch., 38, 851 (1900).
2. Crookes, W., Chem. News, 98, 274 (1908).
3. Vernadskii, V.I. Izvestiya Akad. Nauk (1908).
4. Meyer, R.J., Z. anorgan. Chem., 86, (1914).
5. Goldschmidt, V.M., and Cl. Peters. Zur Geochemie des Scandiums, Nachr. Ges. Wiss. Göttingen, III, No. 14; IV, No. 6 (1931).
6. Tongeren, W., On the occurrence of rare elements in the Netherlands East Indies, Amsterdam (1938).
7. Oftedal, I., Norsk. geol. tids. skr. 23, (1943).
8. Dudykina, A.S., Zakonomernosti Raspredeleniya Skandiya v Porodakh i Mineralakh na Territorii SSSR (Regularities in the distribution of scandium in rocks and minerals on the territory of the USSR) IGEM AN SSSR, Moscow, No. 1 (1958).
9. Borisenko, L.F., V sb. tr. IMGRE AN SSSR. Voprosy Mineralogii, Geokhimii i Genezisa Redkometal'nykh Mestorozhdenii (In the book: Problems of Mineralogy, geochemistry and genesis of rare metal deposits) Izd. Akad. Nauk USSR, No. 1 (1957).
10. DeVore, G., J. Geol. 63, No. 4 (1955).
11. Holleck, L., and W. Noddack, Angew. Chemie 50, No. 43, 819 (1937).
12. Yatsimirskii, K.B., and V.P. Vasil'ev. Konstanty Nestoikosti Kompleksnykh Soedinenii (Dissociation constants of complex compounds) Izd. Akad. Nauk SSSR, p. 1 (1959).
13. Sterba, J.S. Böhm - Casopis Ceskoslov. Lekarnictwa 17, 301 (1937).

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BEHAVIOR OF TIN AND INDIUM IN THE COLLOFORM AGGREGATES OF CASSITERITE FROM THE DZHALINDA DEPOSIT OF MALYY KHINGAN

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(ABSTRACT)

On the basis of the chemical investigations it was established that cassiterite collomorph aggregates of the Dzhalinda deposit contain some acid saturated tin not associated with sulphur.

It was discovered that in cassiterite collomorph aggregates indium is found in the form of various independent compounds. Some indium compounds are easily soluble in mineral acids (H_2SO_4, HCl) whereas the others are stable.

The authors suppose, that acid stable indium compounds are indium-arsenic minerals and easily soluble ones are oxidic minerals.

The Dzhalinda tin deposit belongs to the group of the so-called "wood tin" deposits genetically related to acid extrusives. The mineralization is localized in the fracture zone of Upper Cretaceous rhyolite which had undergone intensive hydrothermal alteration--silicification, sericitization, and kaolinization.

The ore bodies are small irregular pods and lenses and thin veinlets terminating very abruptly along dip and strike. The ore is cassiterite in typical colloform aggregates of colloidal origin. The spheroidal, reniform, and botryoidal masses of cassiterite are composed of alternating concentric bands differing in color and measuring from a few millimeters to fractions of a millimeter in width. The structure of these aggregates was discussed in detail in another paper [4].

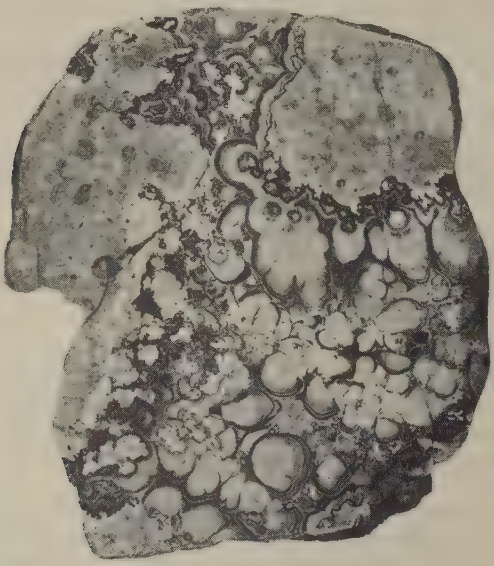
The ore contains small amounts of sulfides (galena, chalcopyrite, pyrite) which can be seen sometimes as minute dot-like segregations in the very thin fractures traversing the colloform cassiterite aggregate.

A spectrographic study of the colloform cassiterite made in the Far East Geological Administration and in the Institute of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), showed that the Dzhalinda cassiterite is distinguished by a high indium content of up to 2%.

New interesting data were obtained from a detailed chemical study of the Dzhalinda ore, which throw light on certain features of the behavior of tin and indium in colloform cassiterite aggregates.

The outer and inner bands of the colloform cassiterite, different in color and degree of crystallization, were selected for analysis. Inasmuch as wood tin sometimes contains acid-soluble tin compounds, chemical analyses were made by the method of Yu. N. Knipovich, L. I. Chuenko and V. M. Krasnikova [3], which, according to these authors, enables one to determine separately 1) the easily soluble tin oxides, 2) the tin sulfide (stannite), and 3) cassiterite.

The method consists in treating the material with sulfuric acid of different concentrations. The treatment lasts 1 hour and is carried out at the temperature of separation of sulfur trioxide fumes. The dilute sulfuric acid dissolves the tin oxides and the concentrated acid dissolves the less soluble tin sulfide. Cassiterite is determined on the insoluble residue remaining after the treatment with concentrated acid.



Colloform cassiterite cementing
fragments of fractured quartz porphyry.
Polished surface (x1.5)

As a result of analysis by this method (see table), it was found that material from the black bands has the maximum content of tin soluble in concentrated sulfuric acid, 0.983% (analysis 1). In recalculating this tin to stannite, a deficiency of copper was discovered. The available 0.38% Cu can fix only 0.36% Sn as stannite, and therefore more than 0.6% of the tin soluble in concentrated sulfuric acid must exist in some other form. Moreover, as the table shows, the material from the light bands (analysis 3) contains tin soluble in concentrated sulfuric acid but does not contain sulfur.

To check whether the tin soluble in concentrated sulfuric acid forms sulfides, the black bands were analyzed by the method of L. V. Zverev and N. V. Petrova [2]. These authors showed experimentally that, by treating tin ores with bromine in carbon tetrachloride, tin sulfides can be completely separated from tin oxides.

Our investigation carried out by this method shows that there are no tin sulfides in the black bands of the colloform cassiterite from Dzhalinda.

As for the easily soluble tin oxides, it can be seen from the table that the amount of tin dissolved in dilute sulfuric acid is approximately the same in the different bands, ranges from 0.108–0.116% and is independent of sulfur content.

The data on the acid-soluble tin suggest that the colloform cassiterite aggregates contain sulfur-free tin compounds soluble in sulfuric acid which are not detected by microscopic examination. The possibility is not excluded that the acid-soluble tin is derived to some extent from the decomposition of colloform cassiterite by sulfuric acid.

In the table of analyses, attention is attracted by the very high indium content, amounting to 1.35%. Indium is a rare element and its maximum content in minerals as recorded in the literature only rarely rises to 1%. The total indium content in the colloform cassiterite varies considerably among the different bands, and this agrees with N. M. Prokopenko's observation that the indium content in sphalerites varies sharply even within a single deposit.

As a result of a chemical phase analysis, it was found that indium occurs in the colloform cassiterite in several forms. Under treatment with ulfuric acid of different concentrations, indium behaves as follows:

The black bands of colloform cassiterite contain 1.11% indium, and more than 96% of its total content is retained in the insoluble residue with ess than 4% going into the acid solution.

In the light-colored bands (analyses 2 and 3) this proportion is substantially different. In the third analysis, the insoluble residue contains 4.65% of the total indium, while almost half of it has gone into solution in dilute sulfuric acid. In the second analysis, the insoluble residue retains nly about 3% indium and the rest, more than 97% is dissolved in dilute ulfuric acid. Finally, in the fourth analysis of mixed bands, about 90% of he indium passes into the acid solution. Thus, excluding the first analysis, f the material from the black bands, from 97.45 to 90% of the total indium asses into dilute sulfuric acid solutions.

The concentrated sulfuric acid treatment of the different concentric ands extracted only small amounts of indium (analyses 1 and 3) and in one ase (analysis 2) none at all.

It should be emphasized that no connection is observed between the content of tin and indium in the colloform aggregates of cassiterite. For instance, analyses 2 and 4 show nearly the same tin content, but in the ormer the content of indium is two times as high. It is easily apparent

Chemical Analyses of Colloform Cassiterite

Elements		Analysis 1	Analysis 2	Analysis 3	Analysis 4
		analyzed zones			
		black	yellow-gray	gray	mixed
Sn, % by wt.	Total	69.63	73.44	74.563	73.50
	In residue insol. in conc. H_2SO_4	68.54	73.082	74.30	72.73
	In conc. H_2SO_4 solution, sp. g. 1.84	0.983	0.242	0.149	0.77
	In dilute H_2SO_4 solution (1:3)	0.107	0.116	0.108	n. d.
	Tin from residue insol. in conc. H_2SO_4 recalculated to cassiterite	86.97	92.74	94.29	92.3
In, % by wt.	Total	1.11	1.35	0.58	0.66
	In residue insol. in conc. H_2SO	1.072	0.04	0.317	0.07
	In conc. H_2SO_4 solution, sp. g. 1.84	0.021	none	0.002	0.58
	In dilute H_2SO_4 solution (1:3)	0.017	1.31	0.261	n. d.
	Amount of indium in residue insoluble in conc. H_2SO_4 in % of its total content	96.4	2.97	54.65	10.6
	As	3.19	0.12	0.54	0.47
	S (total)	0.62	0.21	0.02	0.66
	H_2O ±	0.69	0.44	0.17	n. d.
	Zn	0.50	0.24	0.19	0.08
	Pb	0.095	trace	trace	0.09
	Cu	0.38	trace	trace	n. d.
	Bi	0.003	0.0011	0.002	n. d.
	MnO	0.39	1.24	1.02	0.26
	Fe_2O_3	1.41	0.93	0.69	1.12
	Al_2O_3	1.28	1.38	1.24	1.17
	SiO_2	3.48	1.39	1.54	3.34
	Sb	trace	none	trace	0.05
	Mo	n. d.	n. d.	n. d.	0.002

Note: n. d. = not determined.

also that the amount of indium dissolved by sulfuric acid from the different bands of colloform cassiterite does not depend on the amount of acid-soluble tin.

The data indicate that indium is not a diadochic substitute in cassiterite but is present in it both in stable compounds and in compounds easily dissolved in sulfuric acid.

Our investigations show that the indium compounds easily soluble in sulfuric acid are soluble also in dilute hydrochloric acid. The cassiterite from the light bands, which contains 1.35% indium, was treated first with dilute and then with concentrated hydrochloric acid (at the boiling temperature of HCl). Almost the entire indium content, except for 0.01%, was dissolved in dilute hydrochloric acid.

The indium compounds easily dissolved in acids are present mainly in the light-colored bands of colloform cassiterite. According to the table, the indium content in these bands does not depend on the content of the easily soluble tin compounds (analysis 2) nor on the content of arsenic (analysis 2) or sulfur (analysis 3). Nor is indium united with manganese, for in the treatment of cassiterite with dilute hydrochloric acid it was discovered that, unlike indium, manganese does not pass into solution. It may be supposed on the basis of the analyses that indium is present in the light-colored bands in the form of easily soluble oxides.

Let us consider the form of occurrence of indium in the black bands of the colloform cassiterite. According to the chemical analyses the black bands contain over 13% impurities. Evidently they are composed of finely crystalline cassiterite intimately intergrown with finely dispersed minerals which cannot be resolved by the usual optical methods. The x-ray analysis of the black bands shows quartz associated with cassiterite.

In the treatment of the black bands with concentrated sulfuric acid, more than 1% of indium is retained together with cassiterite in the insoluble residue. High concentrations of indium in the form of diadochid admixture are not typical of cassiterite. S. V. Bleshinskii and V. F. Abramov [1] refer cassiterite to the group of minerals with an average indium content of 0.01-0.05%.

Evidently in the black bands indium does not enter into the lattice of the microcrystalline cassiterite but forms an independent mineral stable in sulfuric acid. It is difficult to believe that in the alternating concentric bands of colloform cassiterite indium is present in the black bands entirely in the cassiterite lattice, and in the light bands, in the form of an easily soluble compound.

At the same time, an interesting feature of the composition of the black bands should be mentioned: they are characterized by a very high arsenic content reaching 3.19%. Our investigations show that a part of the arsenic is united with iron and forms arsenopyrite and loellingite.

After treatment of the cassiterite from the black bands with nitric acid, arsenic and indium are found in the insoluble residue, but, as is well known, arsenopyrite and loellingite are decomposed by nitric acid. This suggests that in the black bands indium occurs as an indium-arsenic compound.

The possibility of reaction between indium and arsenic in aqueous solutions was pointed out by A. T. Nizhnik [5] and by D. M. Chizhikov et al. [7].

Thus, it is quite possible that during the formation of the Dzhalinda deposit, an indium-arsenic mineral, together with cassiterite, was precipitated from the ore-bearing solutions containing arsenic, indium, tin, and other elements.

In conclusion we must state again that:

1) The colloform aggregates of cassiterite contain acid-soluble tin compounds free of sulfur. It is possible that some of these are hydrous tin oxides.

2) Indium in the colloform cassiterite aggregates occurs in compounds, some of which are stable and others easily soluble in inorganic acids (H_2SO_4, HCl).

3) The insoluble indium compounds may possibly be indium-arsenic minerals, while the easily soluble ones are most likely oxides.

REFERENCES

1. Bleshinskii, S. V., and V. F. Abramova, Khimiya Indiya (Chemistry of indium) (1958).
2. Zverev, L. V., and N. V. Petrova, Zavodsk. labor., No. 12 (1957).
3. Knipovich, Yu. N., L. I. Chuenko, and V. M. Krasnikova, Uskorennye Metody Opredeleniya Olova i Fazovyi Analizis Olovyannykh Rud. V kn. "Khimicheskie i Fiziko-khimicheskie Metody Analiza Mineral'nogo Syr'ya" (Rapid methods of determination of tin and phase analysis of tin ores. In the book: Chemical and physico-chemical methods of analysis of mineral raw materials), (1955).
4. Komarova, G. N. Geologiya Rudnykh Mestorozhdenii, No. 2 (1959).
5. Nizhnik, A. T., Ukr. khim. zh. 22, No. (1956).
6. Novorossova, L. E., Ob Opredelenii Indiya v Rudakh Soderzhashchikh Olovo. V kn. "Soveshchanie po Metodam Opredeleniya Rasseyannykh Elementov v Rudakh i Produktakh Ikh Pererabotki" (On determination of indium in ores containing tin. In the book: Conference on determination of trace elements in ores and products derived from them), Moscow, Inform. No. 194, p. 49 (1956).
7. Chizhikov, D. M., N. A. Gurovich and G. M. Denisova, Zh. priklad. khimii 29, No. 5 (1956).

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DISTRIBUTION OF BROMINE IN THE ROCK SALT OF THE ANGARA-LENA SALT BASIN AND THE POSSIBILITY OF FINDING POTASSIUM SALTS

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(ABSTRACT)

The comparison of the values of the bromine-chlorine coefficient with the scale of normal bromine contents in crystallization products of sea water, according to the data of M. G. Valiashko, is used as a prospecting method.

The direction in which the most prospective region of potassium and magnesian salt deposits most possibly is situated is established according to the values of the bromine-chlorine coefficient for rock-salt in separate pit-holes of the Angara-Lena salt basin.

During the evaporation of sea water, bromine does not form independent minerals but enters into the chlorides. The first chloride to crystallize from sea water is halite, later joined by sylvite, which changes into carnallite or kainite. At the very last stage of crystallization, these minerals are joined by bischofite.

After studying the distribution of bromine in the products of evaporation of sea water, M. G. Valyashko [1, 2] established a scale of normal content of bromine in the precipitated chlorides. Valyashko's scale is shown in Fig. 1. In the first halite crystals the bromine-chlorine coefficient is $0.1 \cdot 10^{-3}$. In the very last crystals, it is $1 \cdot 10^{-3}$, i.e. ten times as high as in the first crystals. The knees on the curve of variation of the bromine-chlorine coefficient correspond to the appearance of new solid phases. The first knee corresponds to the beginning of crystallization of sylvite and the second to the beginning of separation of carnallite. Using the scale of normal bromine content in halite, it is possible, by the mangitude of the bromine-chlorine coefficient, to determine the field of crystallization of sea water in which a given salt deposit was formed. When the distribution of individual fields of crystallization is known, predictions can be made as to the possibility of the occurrence of other salts among the beds of rock salt. If the bromine-chlorine coefficient in halite is $0.3 \cdot 10^{-3}$ or higher, it was precipitated (Fig. 1) in the field of crystallization of potassium salts and hence there is a possibility of finding potassium deposits. Thus, the bromine content in salt deposits may be used as a prospecting guide.

By determining the bromine-chlorine coefficient in rock salt samples from the Angara-Lena basin, the author undertook to establish the field of crystallization of these salt beds and draw conclusions as to the possibility of finding potassium and magnesium salts among them.

Cores from the boreholes (Usol'sk, Polovinkino, Tyret, Zayarsk and others) were used for determining the bromine-chlorine coefficient of the salt beds. Average samples were obtained from the cores by drilling 10 mm holes in the cores. The fragments were collected, powdered and analyzed chemically. The K^+, Mg^{2+}, and SO_4^{2-} ions were determined gravimetrically, the Ca^{2+} and I^- ions, volumetrically, the Cl^- and Br^- ions, potentiometrically, and HBO_2^- and F^-, colorimetrically.

The results of determination of bromine and potassium and the variation in the bromine-chlorine coefficient in rock salt samples from the Usol'sk borehole are presented graphically in Fig. 2. The bromine and potassium contents and the bromine-chlorine coefficients are plotted as abscissas and the depths of the samples as ordinates. In constructing the graph, salts containing not more than 10-15% of insoluble residue were used. The bromine content in the Usol'sk borehole ranges from 0.013 to 0.049%. The average bromine content in the borehole is 0.0269%. The graph shows that the bromine content in the salt beds increases at first, and upon reaching maximum at the depth of 830 m begins to decrease. For the sake of clarity, the points of maximum and minimum bromine content are connected by lines.

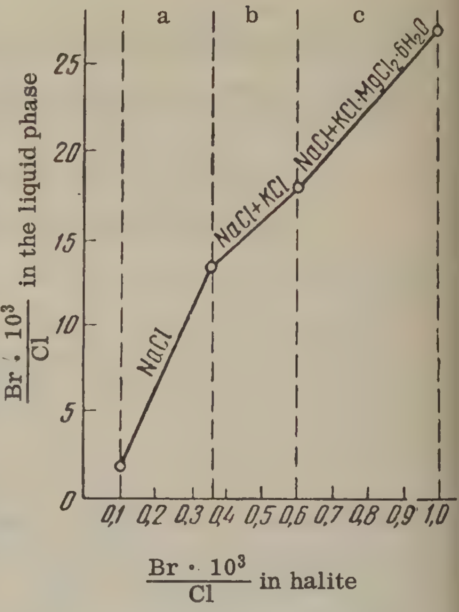

Fig. 1. Scale of normal bromine content in halite after M. G. Valyashko's data

a - field of crystallization of halite,
b - field of crystallization of halite and sylvite,
c - field of crystallization of halite and carnallite

It should be noted that the samples with high bromine content have also a high potassium content (Fig. 2). In the Usol'sk borehole the samples taken at the interval between 760 and 900 m contain from 0.02 to 0.47% potassium, while other samples from the same borehole contain between 0.001 and 0.28% K.

The variation of the bromine-chlorine coefficient with the depth of the

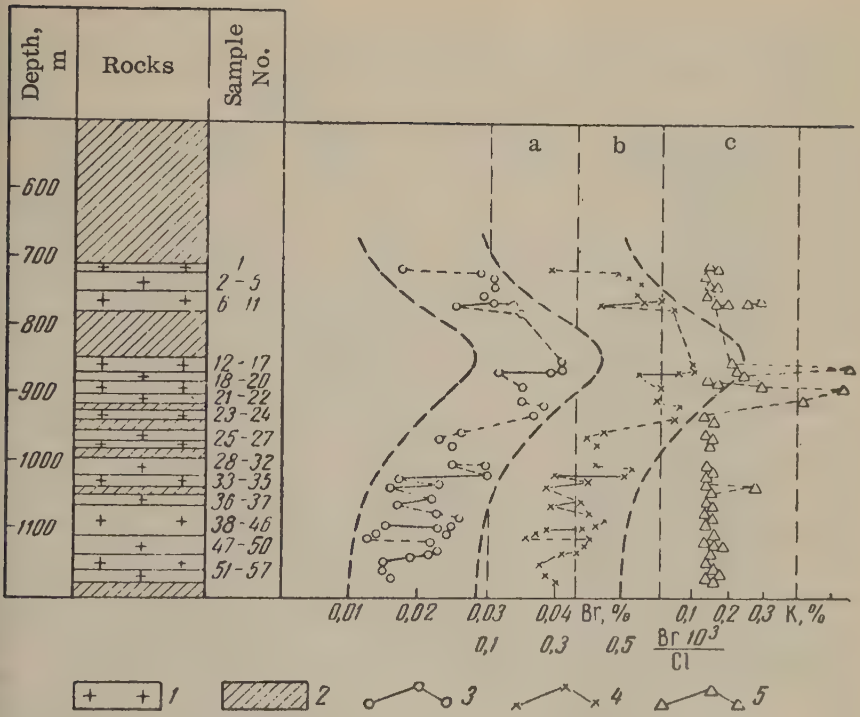

Fig. 2. Variation in the bromine-chlorine coefficient and bromine and potassium content in the samples of rock salt from the Usol'sk borehole ZR

1 - rock salt, 2 - dolomites, limestones, gypsites, anhydrites, 3 - bromine content, in the rock salt samples, %, 4 - bromine-chlorine coefficient, 5 - potassium content in the samples of rock salt, % (a, b and c the same as in Fig. 1)

salt beds also is shown in Fig. 2. The bromine-chlorine coefficient in the salt samples from the Usol'sk borehole varies from $0.22 \cdot 10^{-3}$ to $0.85 \cdot 10^{-3}$, the average being $0.44 \cdot 10^{-3}$. It follows from the graph that the variation of the bromine-chlorine coefficient with depth parallels the variation in the bromine content.

These regularities in the variation of the bromine-chlorine coefficient and the bromine content in rock salt samples from the Usol'sk borehole ZR are observed also in other Usol'sk boreholes (Fig. 3) and in the Kutulik (Fig. 5), Tyret (Fig. 4), Polovinkino, Atovsk, Balykhtinsk, Zayarsk, and other boreholes. The difference is only in the depth at which the bromine-chlorine coefficient reaches its maximum value. The averaged maximum values of the coefficient and the corresponding depths for individual boreholes of the Angara-Lena salt basin are given in the table.

The variation in the bromine content with depth in the individual boreholes of the Angara-Lena salt basin confirms Valyashko's conclusion [1]

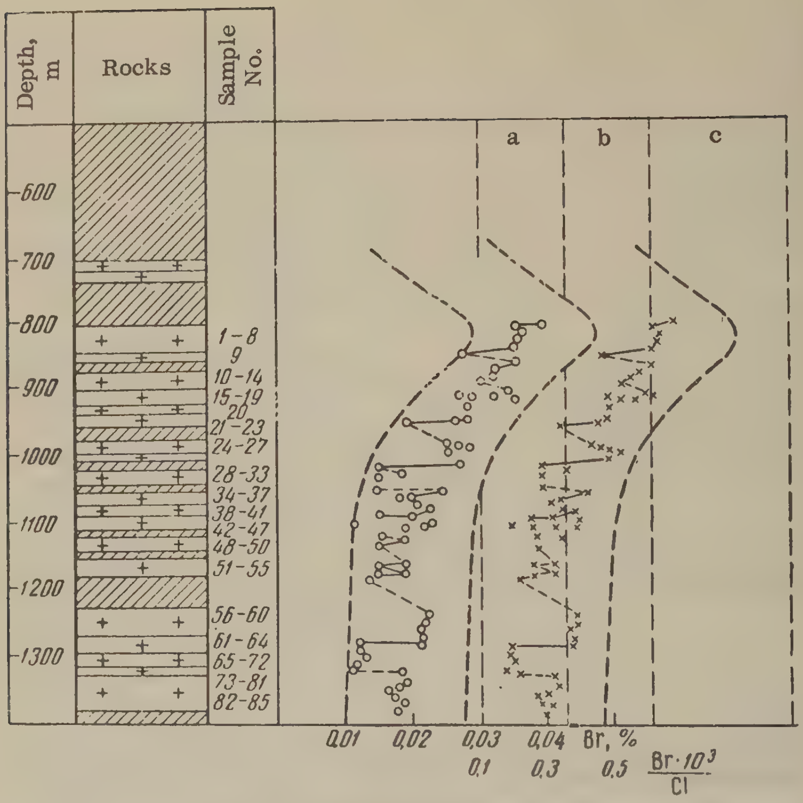

Fig. 3. Variation in bromine-chlorine coefficient and bromine content in the samples of rock salt from the Usol'sk borehole No. 9 (a, b and c as in Fig. 1)

Averaged Maxima of Bromine-Chlorine Coefficient for the Boreholes of the Angara-Lena Salt Basin

Name of boreholes	Number of investigated boreholes	Averaged maxima of bromine-chlorine coefficient	Depth in meters corresponding to the maxima of bromine-chlorine coefficient
Usol'sk	10	$0.54 \cdot 10^{-3}$	830
Polovinkino	2	$0.56 \cdot 10^{-3}$	880
Kutulik	1	$0.40 \cdot 10^{-3}$	1225
Tyret	9	$0.64 \cdot 10^{-3}$	1250
Atovsk	1	$0.59 \cdot 10^{-3}$	1700
Balykhtinsk	2	$0.54 \cdot 10^{-3}$	1280
Zayarsk	1	$0.40 \cdot 10^{-3}$	2200

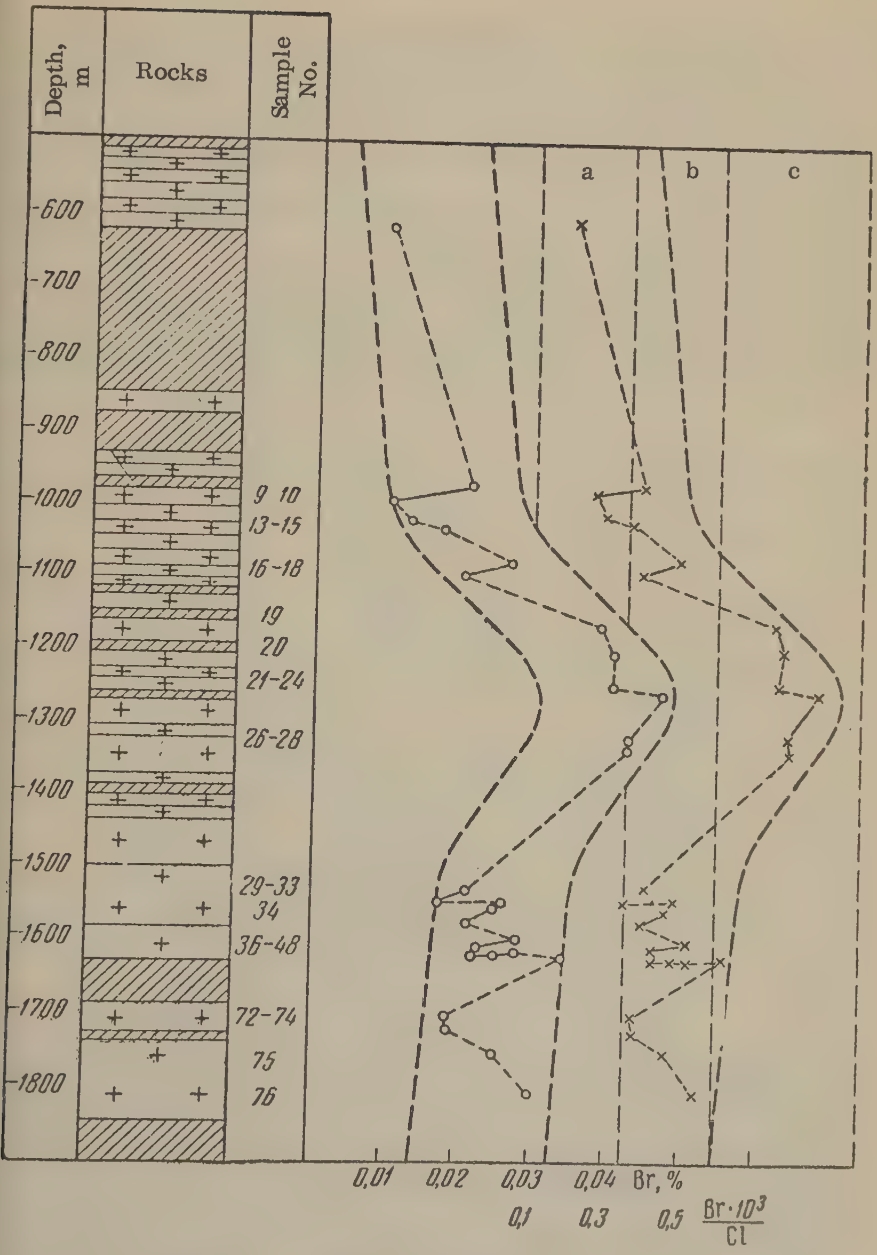

Fig. 4. Variation in bromine-chlorine coefficient and the bromine content in the samples of rock salt from the Tyret borehole No. 1 (a, b and c as in Fig. 1)

that the bromine content in the early portions of the precipitated chloride is low and increases as the evaporation of sea water continues. Therefore, the deepest salt beds will have the lowest bromine content, and it will increase upwards. This is precisely what the graphs show (Figs. 2, 3, 4, 5), except at the very top of the curves. The lack of regularity in the distribution of bromine in the upper salt beds may be explained by the recrystallization of the salts.

Using Valyashko's scale of normal distribution of bromine in halite [1], the author outlined by interrupted lines in Figs. 2, 3, 4 and 5 the fields of crystallization of halite, halite and sylvite, and halite and carnallite. The graphs show that practically all points indicating the bromine-chlorine coefficient in the investigated boreholes fall in the field of crystallization of normal halite and only a few points lie in the sylvite and carnallite fields. The presence of salt beds with a bromine-chlorine coefficient corresponding

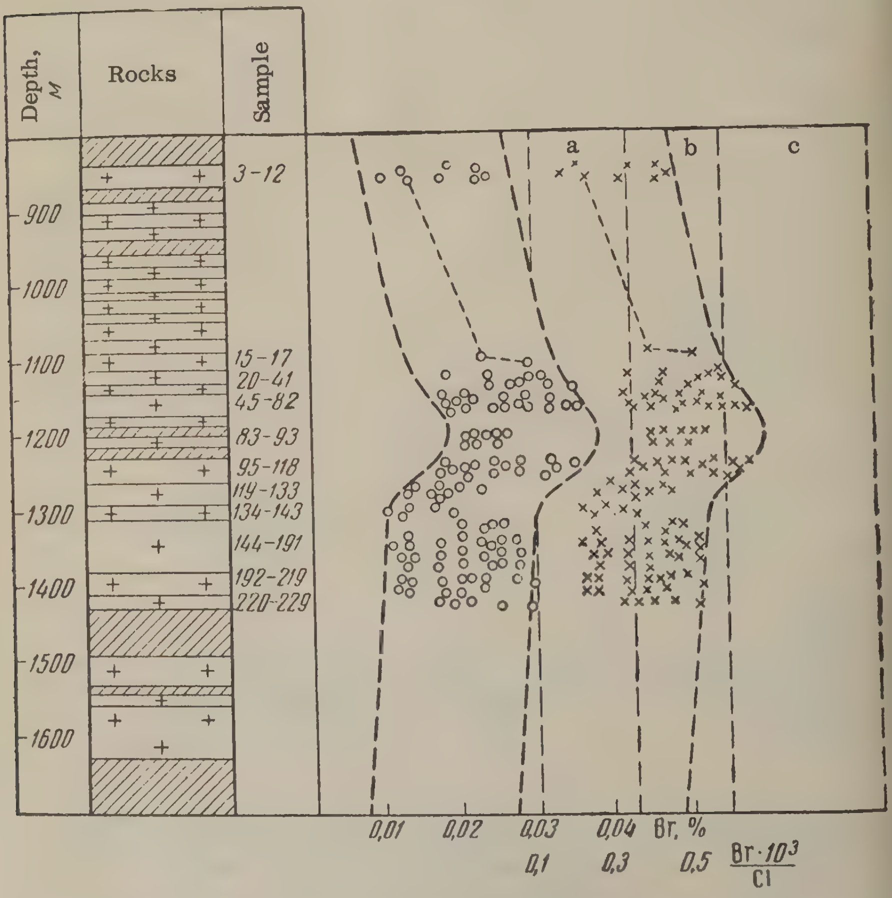

Fig. 5. Variation in bromine-chlorine coefficient and bromine content in the samples of rock salt from the Kutulik borehole No. 4 (a, b and c as in Fig. 1)

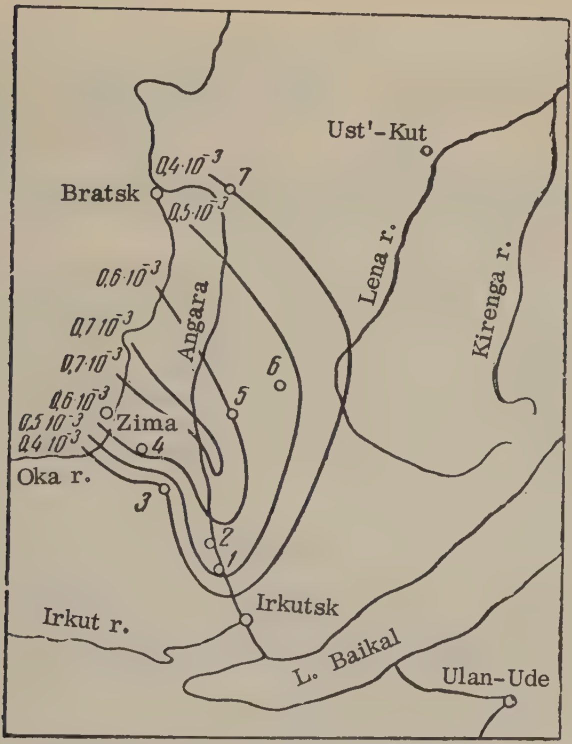

Fig. 6. Distribution of bromine-chlorine coefficient in the salt beds of the Angara-Lena salt basin

1 - Usol'sk boreholes, 2 - Polovinkino boreholes, 3 - Kutulik boreholes, 4 - Tyret boreholes, 5 - Atovsk boreholes, 6 - Balykhtinsk boreholes, 7 - Zayarsk boreholes

the fields of crystallization of halite and sylvite. and halite and carnallite dicates the probability of precipitation of potassium salts and the possi- lity of the occurrence of potassium deposits.

The variation of the bromine-chlorine coefficient from one borehole in a ven deposit to another makes it possible to point out the most promising rea for finding potassium deposits. To do this, the averaged maxima of e bromine-chlorine coefficient (Table) are plotted on a map showing the cation of the boreholes. If there is a sufficient number of boreholes in a gion, then the lines connecting equal values of the bromine-chlorone co- icient would give a clear picture of the variation of the bromine-chlorine efficient. From the data available to the author, orientation contours of ual value of the bromine-chlorine coefficient can be drawn (Fig. 6). The p shows that the values of the coefficient increase to the northwest from Usol'sk boreholes, and it is in that direction, therefore, that the most omising area for discovery of potassium and magnesium salts must lie.

Summary

The bromine content in the rock salt samples from all investigated boreholes ranges from 0.0059% to 0.0490%, and the bromine-chlorine coefficient, from $0.1 \cdot 10^{-3}$ to $0.85 \cdot 10^{-3}$. In all boreholes a definite regularity is observed in the variation of the bromine content and the bromine-chlorine coefficient with depth. At first the bromine content and the coefficient increase, but after reaching a maximum at a definite depth (830 m for the Usol'sk boreholes), they begin to decrease.

The plotting of the values of the bromine-chlorine coefficient on the scale of normal bromine content in the crystallization products of sea water constructed by Valyashko suggests a method for locating deposits of potassium and magnesium salts.

The values of the bromine-chlorine coefficient in the rock salt in the individual boreholes of the Angara-Lena salt basin increase to the northwest of the Usol'sk boreholes, and it is in that direction, therefore, that the most promising area for finding potassium and magnesium salts must lie.

REFERENCES

1. Valyashko, M. G., and T. V. Mandrykina, Brom v Solyanykh Otlozheniyakh Kak Geneticheskii i Poiskovyi Priznak (Bromine in salt deposits as a genetic and prospecting criterion). Trudy VNIIG, Vol. 23 (1952).
2. Valyashko, M. G., Geokhimiya, No. 6, (1956).

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Short Communications

THE COLOR OF AMAZONITE

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As was shown by Zavaritskii [1], the green color of amazonites is of pigenetic origin related to the last stages of the pegmatitic process. He ntroduced the term "amazonitization." At present it is known that this is . large scale process which may affect entire granite massifs. Amazonites re characterized by high rubidium and thallium content [2, 3] and some uthors have noted their high lead content [4, 5, 6]. However, up to now he characteristic metasomatic process, always related in some way to lbitization and recognized by the green coloration it causes, has not been tudied geochemically. The nature of the color itself is also unknown. We hall mention briefly some of the works devoted to this question.

V. M. Goldschmidt, A. N. Zavaritskii, N. P. Kapustin and others [2, 1,] believed that the color of amazonite is due to the diadochic replacement f potassium by rubidium in the structure of microcline. E. N. Eliseev [8] upposed that the green color is due to the presence of Fe^{2+} ions. The loss f color on heating was explained by the oxidation of ferrous iron to ferric.

It is shown in N. P. Kapustin's work that there is a direct proportionality etween the absorption of light by amazonite in the 500-550 mμ region and s rubidium content. But it is well known that color in general is due to elective absorption of light in thosr regions of the spectrum to which the olor of the object is complementary. For bluish-green or green amazonite e region of absorption must be in the orange-red part of the spectrum ith wave lengths of 630-640 mμ. Evidently the coefficients of absorption btained by Kapustin do not explain the green color of amazonite. Morever, it is known from a number of investigations [9, 10] that some unolored microclines contain more rubidium than amazonites.

According to E. N. Eliseev the decolorization of amazonite is accompaied by change of Fe^{2+} to Fe^{3+}, and the mineral becomes yellow or brown. tedal's investigations [11] and our own experiments show that a number intensively colored amazonites from East Transbaikalia, Kola Peninsula, rway and Madagascar become white on heating, without any yellow or own tinge. In view of these facts it was decided to study the geochemistry amazonitization and especially the behavior of lead and the possibility of onnection between it and the color of amazonite, because these questions not been touched upon by previous investigators. For this purpose, azonites and microclines from 12 localities in the USSR and abroad were estigated.

Table 1

Sample No.	Locality	Brief description of partly amazonitized specimens	Content of Pb · 10^{-2}%
29-a	South Urals, Ilmen Mts., pegmatite	Blue area	2.8
29-a	South Urals, Ilmen Mts., pegmatite	White area	1.3
66-a	Kola Peninsula, Keivy, pegmatite	Emerald green area	8.3
66-b	Kola Peninsula, Keivy, pegmatite	Pale blue area	2.6
71	Kazakhstan, Maikul', feldspar veinlets in amazonite granite	Green amazonite	3.9
72	Kazakhstan, Maikul', feldspar veinlets in amazonite granite	Pink microcline	2.8
79-a	South Urals, Ilmen Mts., pegmatite	Green area	2.2
79-b	South Urals, Ilmen Mts., pegmatite	Yellow area	1.6
61	Northern Karelia, pegmatite veins	Cream-colored microcline	0.8
62	Northern Karelia, pegmatite veins	White microcline	0.7

Lead was determined by quantitative spectrography [12] to within about ± 10%. For control, a number of samples were analysed colorimetrically by the dithizone method. The difference in the results of the two methods did not exceed 10-15%. Twenty seven amazonite samples were analyzed, including four samples of partially amazonitized microcline and two common microclines.

The results of the analyses are presented in Tables 1 and 2.

It will be seen from the tables that the amazonites have a fairly high lead content, ranging from 0.009 to 0.083%, and that the more intensively colored specimens have the higher lead content. The lead content in the colored areas is up to 2-3 times as high as in the uncolored areas of the same specimen (Nos. 29, 66, Table 1). Evidently the amazonitization of microcline is accompanied by introduction of lead. To obtain quantitative data on the color of the amazonites, reflection spectra* of 23 specimens were measured in the 400-750 mμ region. For comparison, reflection

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*It would be desirable for this purpose to measure transmission, but the capacity of the specimens, the presence of cracks and inhomogeneities made it impossible to obtain satisfactory absorption spectra.

Table 2

Sample No.	Locality	Brief description of amazonite specimens	Content of Pb · 10^{-2}%	Reflectivity max-min
63	S. Norway, pegmatite	Emerald green	7.7	5.4
78	E. Transbaikalia, Etyka, pegmatite	Bluish-green	7.4	4.9
76	S. Urals, Ilmen Mts., pegmatite	Bright-blue	7.2	5.8
15	E. Transbaikalia, Etyka, pegmatite	Bluish-green	7.0	4.9
26	S. Urals, Ilmen Mts., Pegmatites	Dark green	6.6	4.9
81	"	Dark green	6.6	4.7
80	"	Green	6.1	3.7
86	NW. Baikal region, pegmatite	Bluish-green	4.9	4.2
85	U.S.A., Colorado, pegmatite	Green	4.4	3.5
65	Madagascar, pegmatite	Blue	3.6	2.8
75	S. Urals, Ilmen Mts., pegmatite	Blue	3.5	2.9
82	"	Green	3.0	1.8
84	S. Baikal region, Slyudyanka, pegmatite	Light-green	1.9	1.6
68	Kazakhstan, Kara-oba, pegmatites	Pale green	1.8	0.5
59	S. Urals, Ilmen Mts., pegmatites	Light green	1.8	1.2
64	S. Urals, Ilmen Mts., pegmatites	Light green	1.5	1.2
74	"	Light blue	1.2	0.75
83	N. Mongolia, pegmatite	Pale blue	0.9	1.5
1-E	E. Transbaikalia, Etyka, hydrothermal vein	Light blue	1.0	2.9
77	E. Transbaikalia, Spokoinoe, pegmatite	Light blue	1.7	3.2
1-C	"	Light blue	1.6	3.7
13-E	E. Transbaikalia, Etyka, hydrothermal vein	Blue	1.5	4.0
7-E	"	Blue	2.2	4.6

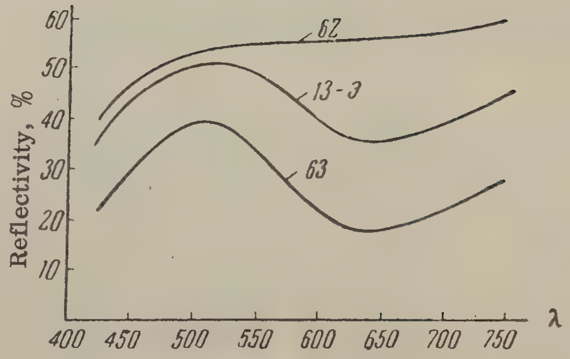

Fig. 1

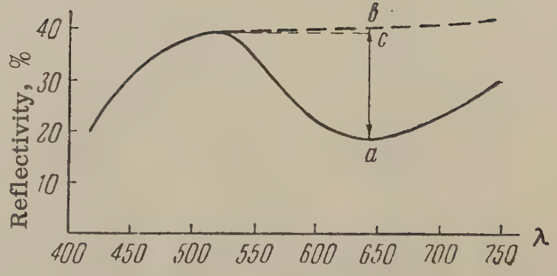

Fig. 2

Fig. 1. Reflectivity curves of amazonites (sp. Nos. 63, 13-E) and white microcline (No. 62)

Fig. 2. Graphic method of determination of the intensity of color in amazonite from the reflectivity curves (solid line -- reflectivity) curve of amazonite, interrupted line -- microcline curve)

spectra of some of the microclines were also measured. The measurements were made on spectrophotometer SF-2M with a polished specimen placed in one of its openings and the standard (freshly powdered magnesium oxide) in the other. The characteristic reflection spectra for two amazonites (No. 63 and No. 13-E) and for white microcline (No. 62) are given in Fig. 1. A comparison of the reflectivity curves of the microclines and amazonites shows that the color of the latter is due to absorption in the 630-640 mμ region.

Because of the difference in the background absorption of the samples, we could not use the absolute values of reflectivity in the 630-640 mμ region. Instead, the difference in the reflectivities of the microclines and amazonites in that region was taken as the characteristic of color intensity. It defines the magnitude of complementary absorption and characterizes directly the intensity of the green color of amazonite (segment ab, Fig. 2). In practice it is more convenient to take the differences between the maximum and minimum on the reflectivity curve (segment ac, Fig. 2) for each specimen. As can be seen from Fig. 2 and the reflectivity curve of specimen No. 62 (Fig. 1), the error introduced by this is slight. The differences between the maximum and minimum reflectivities were determined graphically and are given in arbitrary units (Table 2, Fig. 3).

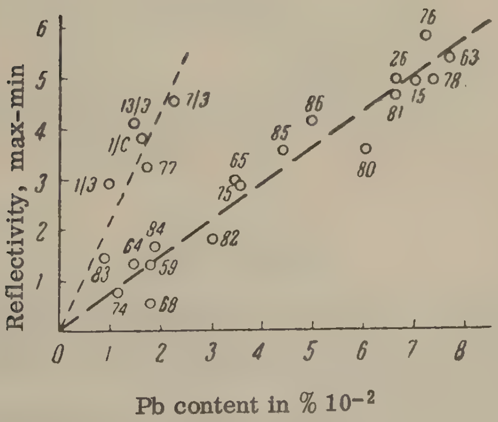

Fig. 3. Dependence of coloration of amazonite on lead content

In Fig. 3 the values characterizing the color (max - min reflectivity) re plotted as the ordinates and the lead content in percent as the abscissas. he 17 specimens from pegmatites show an obvious direct proportionality etween the intensity of color and the lead content. Six specimens are learly separated and lie on another straight line with a steeper slope. hree samples from this group (1-E, 7-E, 13-E) are not pegmatitic but of ydrothermal origin, while the rest of the specimens (1-C, 77, 83) were probably formed under special conditions similar to hydrothermal or hydrothermal.* In general there is a clear relationship between the intensities of color in amazonites and their lead content.

Our experiments in decolorizing amazonites by heating at 500°C and coloring them by x-ray irradiation exclude the possibility of the presence of lead sulfide and indicate that the color of amazonite is due to lattice "defects".

The data presented in this communication indicate that amazonitization is a peculiar, previously unknown type of lead metasomatism. Lead from solutions in which it is evidently rather highly concentrated replaces potassium in the microcline structure. The existence of white microclines also having high lead content (up to 0.04%) suggests a different form of occurrence of lead in amazonites. It is accepted at present that "primary" lead enters into the microcline structure during its crystallization according to the scheme:

$$Pb^{2+}Al^{3+} \rightarrow K^{+}Si^{4+}$$

but when it replaces potassium metasomatically lead probably enters into the lattice according to the exchange reaction:

$$Pb^{2+} \rightarrow 2K^{+}.$$

This type of replacement does not require the high energy needed in breaking the strong Si-O bonds and in what amounts to a complete reconstruction of the structure. Moreover, the entry of lead according to the second scheme is accompanied by formation of cation vacancies, which favors the formation of "defect" color centers.

The present note reports the first results of our investigation. It is proposed to discuss the geochemistry of amazonitization and the color of amazonites in greater detail in a series of special articles.

REFERENCES

1. Zavaritskii, A. N., Zap. Vses. mineralog. o-va, ch. 72, No. 1,(1943).
2. Goldschmidt, V. M., H. Bauer and H. Witte. Sb. Statei po Geokhimii Redkikh Elementov (Collection of papers on geochemistry of rare elements) (1938).
3. Ahrens, L. H., V sb. Redkie Elementy v Izverzhennykh Gornykh Porodakh i Mineralakh (In the collection: Rare elements in rocks and minerals of igneous origin) (1938).
4. Belyankina, E. D., Sb. Voprosy Petrografii i Mineralogii, t. 2 (Collection: Problems of petrography and mineralogy, Vol. 2) (1953).
5. Plamenevskaya, N. L., Trudy IGEM, No. 5, (1957).
6. Oftedal, I., Norsk. geol. Tidsskr. 33, h. 3-4, (1953).

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*Sp. No. 1-C and No. 77 were taken from a quartz-amazonite complex replacing saccharoidal aplite; sp. No. 83 is a large euhedral crystal from a marialitic cavity in a pegmatite.

7. Kapustin, N. P., Izvestiya Akad. Nauk SSSR, ser. geol., No. 3, (1939).
8. Eliseev, E. N., Zap. Vses. mineralog. o-va, ser. 2, ch. 78, No. 1, (1949).
9. Goldschmidt, V. M., Geochemistry, Oxford Press, (1954).
10. Borovik-Romanova, T. F., and A. F. Sosedko. Geokhimiya, No. 5, (1957).
11. Oftedal, I., Mineral. Mag., XXXI, No. 236, (1957).
12. Waring, C. L., and H. Worthing, Amer. Mineralogist 38, No. 9-10, (1953).

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DISCUSSION

ON THE RELATION BETWEEN LITHIUM, SODIUM AND CESIUM CONTENT IN ALKALI BERYLS

A. A. BEUS

A REPLY TO N. V. BELOV'S COMMENTS ON A. A. BEUS' PAPER "THE POSITION OF THE ALKALI METALS IN THE STRUCTURE OF BERYL"

In this reply to N. V. Belov's comments, the author does not intend to defend the infallibility of his conclusions, which, like all other hypotheses of the position of the alkali metals in beryl structure, have not yet been checked experimentally. However, the rich analytical material at our disposal (60, not 6, recalculated analyses of beryl!) makes it possible to point out a number of debatable points in Belov's critical comments which do not give due consideration to the actual peculiarities of composition of alkali beryls.

Apparently all investigators agree that the alkali metal ions in beryl structure may occur in two different positions, some replacing certain ions in the structure (Be, Al) and others occupying the hollow hexagonal channels characteristic of the beryl structure. The channels are probably the only places where such large ions as Cs, Rb and K may be held, and this is also agreed upon by all investigators. Evidently there is no objection to the idea that the smaller alkali ions, Na and Li, may also be located in these channels, especially as all investigators (Belov, Ginzburg, and the author) assume that the replacement proceeds according to the scheme $2R^+ \rightarrow M$ (where M = Be or Al and R^+ = Li, Na, K, Cs) and that half of the alkali ions replace M in the beryl structure and the other half occupy the hollow channels. This fact disposes of Belov's criticism of the "arbitrary" splitting of Li into two groups, for if beryl analyses are recalculated to the formula proposed by him, it becomes necessary to group some of the Li ions with Cs, since in many analyses of lithium-cesium beryls the number of Li ions is considerably in excess of the Be ions supposed to be replaced (short of 3) (Fig. 1). It should be emphasized that Belov's cesium beryl with the ideal composition $Cs(Be, Li)_3Al_2[Si_6O_{18}]$, in which the number of Cs ions is half the total number of alkali ions, has not been found in nature as yet. In the analyses of beryls known to the author the number of Cs ions varies from 0 to 22% of the total number of alkali metal ions.

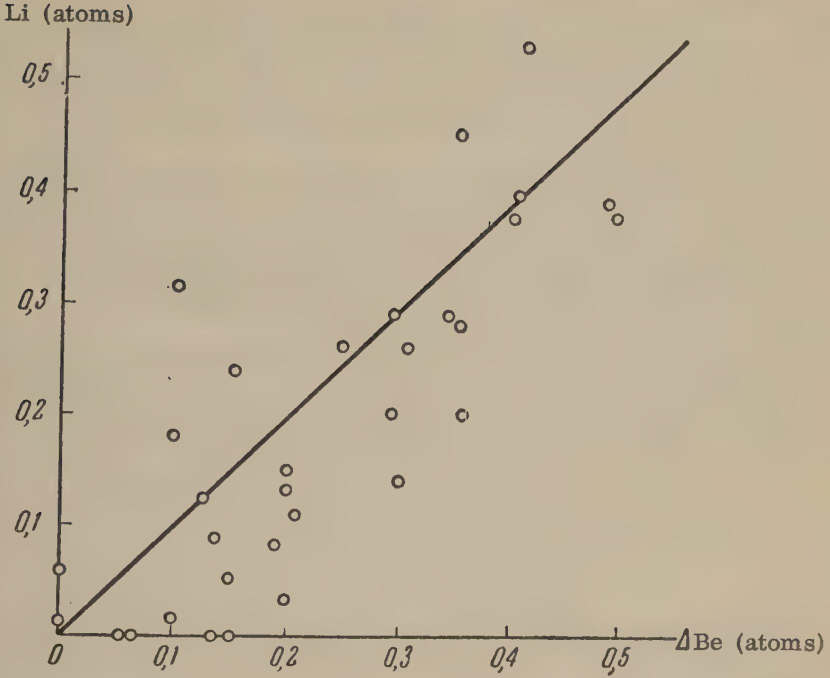

Fig. 1. Absence of clear relation between lithium content and deficiency of beryllium in beryls

The gist of Belov's comments is the proof of crystallochemical affinity between Be and Li needed to justify the formula of alkali beryl proposed by him. It would be possible to accept his arguments if the alkali metals present in beryls in significant amounts were limited to Cs and Li. However, the principal alkali components of the alkali beryls are Li, Na and, to a much less extent, Cs. In discussing the position of Li in beryls, the role of Na cannot be disregarded, for this is tantamount to ignoring the most widespread variety of alkali beryls in which Na is the main, and sometimes practically the only, alkali component. Belov's remark to the effect that in all "new analyses the amount of Na is either equal to that of Li or less" does not agree with facts. Among the 60 analyses of beryls in the author's collection, only three are practically free of alkalies, 15 contain Na only (up to $\mathrm{Na}_{0.25}$ per Si_6) and in 20, Na predominates over Li (from $\mathrm{NaO}_{0.11}$, $\mathrm{Li}_{0.01}$ to $\mathrm{Na}_{0.50}$, $\mathrm{Li}_{0.14}$ per Si_6). Fourteen of these analyses were made in recent years (including number 10, made in the IMGRE, see Table).

The relation between the number of Li ions (per Si_6) in the alkali beryls and the deficiency of beryllium atoms (Δ Be) is shown in Fig. 1.

If Li actually replaced Be in beryls, stoichiometric relations would be reserved between these elements, but in reality they are absent, and Fig. shows that in most analyses the number of Li ions is clearly insufficient to compensate the deficiency of Be. In six cases (of 32 recalculated analyses of lithium beryls) the number of Li ions is noticeably in excess of the number needed to compensate Be deficiency. The points on the diagram of Fig. 1 are widely scattered and do not show any clear relationship between the Li content and the deficiency of Be in alkali beryls. A much clearer relationship exists between the deficiency of beryllium and half the sum of Li + Na + Cs (Fig. 2).

Thus the stoichiometric relations do not argue in favor of the formula proposed by Belov. Often there is not enough Li to compensate the deficiency of Be in the beryl structure and in recalculations Na must be used to supplement Li. As a result, the proponents of the hypothesis of replacement of beryllium in beryl by alkalies must base their hypothesis on the possibility of replacement of beryllium not only by lithium but also by sodium, and to this Belov objects categorically.

On the basis of the well-known resemblance between the structures of beryl and milarite, proved by Belov, the author believes it more probable that both Li and Na, like Ca in milarite, replace Al in beryl in the 6-coordination positions. This does not preclude the possibility of the

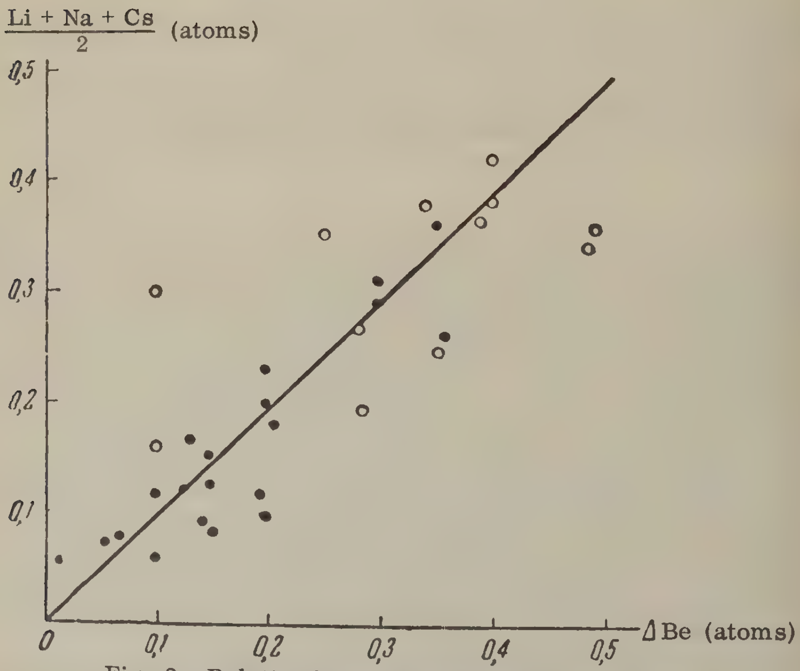

Fig. 2. Relation between deficiency of beryllium and the content of alkali metals in beryls

● -- sodium beryls, o -- sodium-lithium and lithium-cesium beryls

Content of Alkali Cations in Typical Sodium and Sodium-Lithium Beryls With Na in Excess of Li (per Si_6)

Locality and analyst	K	Na	Li	Cs	ΣR+	Be	Al	H_2O
PR, Sinkiang . N. Fedorchuk, 1955	–	0.15	–	–	0.15	2.94	2.02	0.6
"	–	0.16	–	–	0.16	2.93	2.01	0.6
" 1956	–	0.16	0.10	–	0.26	2.84	2.02	0.7
" 1956	0.02	0.28	0.13	–	0.43	2.80	2.02	0.7
" 1956	0.06	0.50	0.14	–	0.70	2.77	2.0	0.8
" 1956	0.02	0.44	0.29	0.05	0.80	2.66	2.07	0.75
PR, Sinkiang . E. Kazakova, 1946	–	0.27	0.15	0.04	0.46	2.80	2.04	0.3
veden, Varuträsk . K. Quensel	0.04	0.22	0.02	0.01	0.29	2.88	2.0	0.5
ola Peninsula . N. Egorova	–	0.22	0.11	0.01	0.34	2.79	1.94	0.5
veden, Varuträsk . K. Quensel	0.02	0.35	0.13	0.01	0.51	2.84	2.07	0.6

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e: CPR represents Chinese Peoples' Republic.

tribution of Li and Na ions remaining after the deficiency of Be has been isfied in the hollow channels characteristic of beryl structure. As for probability of the transfer, in the presence of electropositive alkali s, of a part of Al from the 6-coordinated into the 4-coordinated positions, phenomenon, once investigated in detail by V. S. Sobolev, is very com- n among the silicates.

The author believes that the data cited above on the relationship between content of lithium, sodium and cesium in alkali beryls cannot be used xplaining the position of the alkali metals in beryl structure.

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EXPANDED FORMULAS OF BERYL

N. V. BELOV

The atomic structure of beryl "surrendered" to the crystal chemists very readily, for in the unit cell of the space group $D_{6h}^{2} = P6/mcc$, abounding in symmetry elements, atoms of the formula $Be_3Al_2Si_6O_{18}$ can be distributed according to their characteristics (ionic radius, coordination number) in one way only [1].

In recent years a number of works by Soviet authors (A. I. Ginzburg [2] N. V. Belov [3, 4] A. A. Beus [5, 6]) have been devoted to the problem of possible diadochic substitutions in beryl, but no agreement has been reached in the interpretation of chemical analyses of different natural beryls.

Beus states in his latest paper that he has 60 new analyses at his disposal, and evidently of good quality. He cites 12 of them in sufficient detail, but for the rest he gives statistical data only.

Without repeating what has been said in the two papers by Beus [5, 6] and by me [4], I shall state that with the clearly expressed (in the analyses cited by Beus) stoichiometric ratio (of the number of atoms) Al:Si = 2:6, neither of us wants to take a part (stoichiometric) of Al and cover with it the often observed deficiency in the number of Be ions and then subtract an equivalent part of Li ions from the total Li (whose amount is not the same in the majority of analyses and is not stoichiometric) to fill the gap we made in the two Al atoms of the classical beryl formula.

This is too complex for a natural process which usually follows the simplest course. If according to analysis the deficiency of Be is finally compensated by Li ions, it is not likely that this is accomplished by the entry of Li into the positions of a part of the Al ions and by redistribution of the crowded out Al ions in the Be positions. Reading the analyses directly, we see that Li takes the Be positions, and quickly find an explanation of this in the nuclear reaction

$$2Be \rightarrow 2Li + He. \qquad (A)$$

If in the tetrahedral structure of $(Be_2Si_6)O_{18}$ the Be ions play the "anion" role (are centers of the oxygen tetrahedra), then the same role is played by the Li ions. The "anion" lithium (in tetrahedra) has long been familiar crystal chemists from the example of Na-cryolithionite [7, 3], an analgue of garnet in which the role of LiF_4 is identical with the role of the O_4 tetrahedra in garnets (grossularite - $Ca_3Al_2(SiO_4)_3$ -- cryolithionite $Na_3Al_2Li_3F_{12}$).

The loss of one positive charge in the Be-Si structure as a result of reacement of Si^{4+} by Li^{1+} is compensated (as in the alumino-silicates in the eplacement of Si^{4+} by Al^{3+}) by the entry into the structure of beryl of an lditional univalent cation. The necessary space is provided by the broad npty channels about the sixfold axes which are characteristic of beryl ructure and have a diameter of 2, 6 A. To fill this space the cations must e large. Usually they are Na^+ ions, but more effective as the supplemenry cations, a fact emphasized in "Mineralogies," are the very large (and re) Cs^{1+} ions.

But still earlier the same channels, both the cells containing Be changed to Li and the neutral positions in the neighboring cells had accommodated e uncharged helium resulting from the nuclear reaction (A). Thus the rmula of standard beryl must be written in the form $(He_{\underline{x}})Be_3Al_2Si_6O_{18}$ d the formula of Cs-beryl, or vorobjevite, in the form

$$(He_{\underline{x}-\underline{z}})Cs_xBe_{3-\underline{x}}Li_{\underline{x}}Al_2Si_6O_{18}. \qquad \text{(I)}$$

metimes the "end" member of vorobjevite (see [2]) is written: $s_1Be_2LiAl_2Si_6O_{18}$. In the more common Na-beryls, we have $Ie_{\underline{x}-\underline{z}})Na_{\underline{x}}Be_{3-\underline{x}}Li_{\underline{x}}Al_2Si_6O_{18}$, or, disregarding the helium content:

$$Na_{\underline{x}}Be_{3-\underline{x}}Li_{\underline{x}}Al_2Si_6O_{18}. \qquad \text{(II)}$$

these formulas the loss of one Be atom is compensated by the entry of o univalent cations, the small Li^{1+} which replaces Be^{2+} (with preservan of stoichiometry) and the large Na^{1+}, or even Cs^{1+}, which enter the npty channel and play the same nonstoichoimetric role as He and even O (!).

The ratio (Na+Cs+Li) : (Be ↑) = 2 is very close to 2 (cf. [5, 6]), but rare cases in the presence of excess Al it may deviate in one direction the other, to compensate the deficiency of either Be or Si. In both ses Al goes into the tetrahedra (and this does not require V. S. Sobolev's thority). In the first case (always characteristic of the beryl analogue ilarite) we have the formula (leaving He out and disregarding the possiity of replacement of Na by other large alkali ions):

$$Na_{\underline{x}-\underline{y}}Be_{3-\underline{x}-\underline{y}}Li_{\underline{x}}Al_{2+\underline{y}}Si_6O_{18}. \qquad \text{(III)}$$

d in the second:

$$Na_{\underline{x}+\underline{y}}Be_{3-\underline{x}}Li_{\underline{x}}Al_{2+\underline{y}}Si_{6-\underline{y}}O_{18} \qquad \text{(IV)}$$

e above ratio deviates from 2 in different directions in these two cases.

It follows from Formulas I and II that the amount of Na(Cs) in beryls st equal the amount of Li, and formulas III and IV destroy the slight iations in those accidental cases when the amount of Al is non-stoichiotric. But in the old analyses of beryl given by Ginzburg, and in the 60 new analyses cited by Beus, the sum Na+Cs+K is often greater than the amount of Li, and sometimes the latter is absent. Inasmuch as the direct replacement of Be (ionic radius ∼ 0.30Å) by Na (ionic radius ∼ 1Å) is impossible, Beus circumvents this by allowing Na to crowd a part (stoichiometric) of Al from the octahedra and by making it fill the deficiency of Be in the tetrahedra.

The argument cited in favor of this complicated mechanism is the existence of milarite with a formula analogous to that of beryl:

Beryl	$He_{\underline{x}}Be_3Al_2\ [Si_6O_{18}]$
Milarite	$KBe_2AlCs_2[Si_{12}O_{30}]$.

In milarite, Al and Be do occupy the same positions, but what is important, identical positions in the space group *P6/mcc* are occupied by Al in beryl and by Ca in milarite [8], and this suggests to Beus diadochy between Ca and Al and then between Na and Al (plagioclase). But of course an analogous structure plan does not imply diadochy. There is no isomorphism between NaCl -- MgO -- PbS; moreover, there is no isomorphism between NaCl and AgCl although in this pair not only the plan is the same but so are the lattice parameters, while in beryl and milarite they are quite different (beryl: $\underline{a}$ = 9.21Å, $\underline{c}$ = 9.17Å; milarite: $\underline{a}$ = 10.5Å, $\underline{c}$ = 13.9Å).

The author has shown in detail [9] that beryl and milarite are representatives of two large groups of silicates, one headed by the pyroxenes and the other by the pyroxenoids (wollastonite). The leading cations in the first family are Al, Mg and Fe, and in the second, Ca, Na and RE. There is no isomorphism between the members of the two groups. Aluminum, which plays the role of a cation in the first group, is an anion in the second (in tetrahedra). To speak of diadochy between Al and Na is like assuming identity of their roles in albite. It is doubtful that any chemist (or crystal chemist) would seriously consider diadochic substitution of Na for Al, but in the case of beryl this paradox is not necessary anyway.

The point is that the four formulas I–IV are written with the supposition that in beryl all O, Si, Al and Be positions are occupied "100%" (according to the ideal formula) and only the positions of He (Cs, Na, H_2O) are admitted, in fact are known, to be filled far short of 100%.

But then, why should the less than 100% filling of beryllium positions shown by analyses be interpreted in some special way? If, according to analysis, there is no Li for these positions nor additional Al (always that in excess of Al_2 of the formula), it simply means that the Be positions also are not always filled to 100%. The deficiency of charges in the structure $(Si, Be)O_2$ is compensated by the simultaneous introduction into the channels of two alkali cations -- Na(Cs).

From the point of view of charge balance in the structure, beryl structures are defective, or, more precisely, deficit or "omission structures." This is an old concept in crystal chemistry. The best known illustration of it is pyrrhotite, whose empirical formula, Fe_6S_7, is now written $Fe_{1-\underline{x}}S$, where $\underline{x} \approx \frac{1}{7}$, and is explained by the omission of a part of the Fe ions from the ideal FeS pattern. The balance of charges is attained by the oxidation of a certain number of Fe^{2+} ions to Fe^{3+} and the expanded formula of pyrrhotite reads:

$$Fe^{2+}_{1-\underline{x}}\,Fe^{3+}_{0.67\underline{x}}\,S.$$

Plazolite (hibschite [3]) turned out to be grossularite (grossularoid) vith a third of the tetrahedra which are replaced in garnet, vacant. The harges are balanced by the replacement of a SiO_4 tetrahedron by an $(OH)_4$ etrahedron equal in size and charge.

Exactly the same is the cause of the frequent presence in forsterite Mg_2SiO_4) of over 1% H_2O which leaves the crystal only at a very high emperature. The "paradox" is resolved by an "expanded" formula of orsterite

$$Mg_2[SiO_4]_{1-\underline{x}}(OH)_{4\underline{x}}\ .$$

Accepting on the evidence of 60 analyses of beryls collected by Beus the xperimental fact of the deficiency of ions in the positions normally occupied y Be, and realizing the experimental and theoretical impossibility of the ubstitution Na → Al → Be, we can derive from the 60 analyses of beryl the ollowing formula:

$$(H_2O)_{\underline{u}}He_{\underline{z}}\overset{I}{Me}_{2\underline{x}-\underline{y}}Be_{3-\underline{x}}Li_{\underline{y}}Al_2Si_6O_{18}$$

$$\underset{A}{\underline{[(H_2O)_{\underline{u}}He_{\underline{z}}\overset{I}{Me}_{2\underline{x}-\underline{y}}]}} - \underset{B}{\underline{[Be_{3-\underline{x}}Li_{\underline{y}}]}}Al_2Si_6O_{18}$$

ith incompletely filled positions A and B and with the conditions:

$$\underline{u} + \underline{z} + 2\underline{x} - \underline{y} \leqq 1, \qquad 3 - \underline{x} + \underline{y} \leqq 3.$$

is very seldom that the complicated formula

$$(H_2O)_{\underline{u}}He_{\underline{z}}\overset{I}{M}_{2\underline{x}-\underline{y}-\underline{s}+\underline{t}}\ Be_{3-\underline{x}}Li_{\underline{y}}Al_{\underline{s}}Al_2Si_{6-\underline{t}}Al_{\underline{t}}O_{18}\ .$$

required.

Unfortunately Beus mentions, rather vaguely, that in 12 analyses from s collection the amount of Li exceeds the deficit of Be, and therefore is excess finds its way into the channels, into M^1. I should not like to cept this interpretation, although the possible mechanism of substitution Li for Na was pointed out in the structure of amblygonite solved by monov and myself [10].

Until recently, milarite was a mineralogical rarity known from only one viss locality, but now it has been found on Kola Peninsula [11] and so it ill be possible to check its peculiarities suggested by the above considera- ons: namely, the impossibility of lithium being present in milarite in gnificant amounts (all positions in the channels being already occupied by) and the final fate of milarite, its alteration not into kaolinite but into enite-tobermorite (cf. [9]), the characteristic alteration product of beryl.

REFERENCES

. Bragg, W. L., and J. West, The structure of beryl. Proc. Roy. Soc. 111 A, 691 (1926).

2. Ginzburg, A. I., K Voprosu o Khimicheskom Sostave Berilla (On the chemical composition of beryl), Tr. mineralog. muzeya, No. 7, 56 (1955).
3. Belov, N. V. Ocherki po Strukturnoi Mineralogii (Essays in structural mineralogy), IX, Mineralog. sborn. L'vovsk. geol. o–va, No. 12, 15 (1958).
4. Belov, N. V., Po Povodu Raboty A. A. Beusa "O Polozhenii Shchelochnykh Metallov v Strukture Berilla (Comment on A. A. Beus' paper "On the position of alkali metals in the structure of beryl), Geokhimiya, No. 3, 282 (1959).
5. Beus, A. A. O Polozhenii Shchelochnykh Metallov v Strukture Berilla (On the position of alkali metals in the structure of beryl), Geokhimiya, No. 3 (1959).
6. Beus, A. A., O Zavisimosti Mezhdu Soderzhaniem Li, Na and Cs v Shchelochnykh Berillakh (On the relationship between the content of Li, Na and Cs in alkali beryls), Geokhimiya, No. 5 (1959).
7. Menzer, G. Die Kristallstruktur des Kryolithionits, Z. Kristal. 75, 265 (1930).
8. Belov, N. V. and T. N. Tarkhova. Kristallicheskaya Struktura Milarita (Crystal structure of milarite), Tr. In–ta kristal. 6 83 (1951).
9. Belov, N. V., Ocherki po Strukturnoi Mineralogii (Essays in structural mineralogy), X. Mineralog. sb. L'vovsk. geol o–va, No. 13, 23 (1959).
10. Simonov, V. I. and N. V. Belov. Opredelenie Struktury Ambligonita Metodom Minimalizatsii (Determination of the structure of amblygonite by the method of minimalization), Kristallografiya 3, No. 4 (1958).
11. Sosedko, T. A., Nakhodka Milarita na Kol'skom Poluostrove (Discovery of milarite on Kola Peninsula), Doklady Akad. Nauk SSSR 129, No. 5 (1959).

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THE FEDOROV SESSION ON CRYSTALLOGRAPHY

(40th anniversary of E. S. Fedorov's death)

From May 21 to 27, 1959, scientific meetings were held in Leningrad ommemorating the 40th anniversary of the death (May 22, 1919) of the reatest Russian crystallographer, Evgraf Stepanovich Fedorov. The ıeetings were organized by the International Crystallographic Union, the cademy of Sciences USSR, the Leningrad Mining Institute, and the All- nion Mineralogical Society. About 90 papers were read in 5 general and 4 sectional meetings. The sections included two in crystal chemistry and ıe in electron diffraction. Several hundred persons attended the meeting, mong them many foreign scientists.

Although the meetings were devoted to crystallographic problems, many f the papers were of considerable interest to geochemists. Some of these re reviewed below.

N. V. Belov (Moscow), in his "Chapter two of the crystal chemistry of licates," explained why double tetrahedra $[Si_2O_7]^{6-}$ form instead of inde- endent tetrahedra $[SiO_4]^{4-}$. The cause is the large size of the cations RE, a, and Na, among which the silicon-oxygen anions are distributed. This very well illustrated by milarite, $K[Be, Al]_3 Ca_2[Si_{12}O_{30}]$, whose struc- re may be pictured as that of beryl, $Be_3Al_2Si_6O_{18}$, but with double $i_6O_{18}]$ rings formed because the positions occupied in beryl by the rela- vely small Al ions are taken in milarite by the large Ca ions. The size the pentavalent phosphorus ion is smaller than that of silicon, and so ven the medium-sized magnesium ion is capable of forming the magnesi- n pyrophosphate structure, $Mg_2[P_2O_7]$ containing double tetrahedra $_2O_7]$. In the case of the Al ion, which is larger than the silicon ion, a rge ion such as Ba is required to form double octahedra, $[Al_2O_7]$. The inerals cuspidine, $Ca_4[Si_2O_7]F_2$, and tilleyite, $Ca_5[Si_2O_7][CO_3]_2$, were so discussed by Belov from this point of view.

Belov regards the structure of the wöhlerite-lavenite group as being erivative from the cuspidine structure. The recently discovered seido- erite, $Na_8\ (Zr_3Ti)Ti_2Mn_2O_4 \cdot [Si_2O_7]_4F_2$, which has been investigated ystallochemically also, has this type of structure.

The discovery of this mineral made it possible to evaluate quantitatively limits of diadochy between zirconium and titanium, which occurs in ite of the fact that the difference between their ionic radii, $Zr^{4+} \approx$ 87 Å and $Ti^{3+} \approx 0.64$ Å, is 36% (instead of 15%!) of the radius of the aller ion. If, as Belov believes, there is a shift to the right in the oxi- tion-reduction equilibrium, $Ti^{4+}Mn^{2+} \rightleftarrows Ti^{3+}Mn^{3+}$ ($Ti^{3+} = 0.83$ Å and

Mn^{3+} = 0.71Å), then not only the diadochy between Ti^{4+} and Zr^{4+} becomes understandable, but also between Mn and Mg. The peculiarities of β-wollastonite structure, which contains $[Si_{2+1}O_9]$ ∞ chains, were also discussed by Belov. The joining of two pyroxene chains, $[Si_2O_6]^{4-}$, gives the double amphibole chain $[Si_4O_{11}]^{6-}$, and in the same way the joining of two $[Si_3O_9]^{6-}$-chains forms $[Si_6O_{17}]^{10-}$ xonotlite bands. He reviewed not only the structure of xonotlite but also those of other related silicates. In connection with the structure of wollastonite, Belov discussed the structure of rhodonite, in which a new type of metasilicate chain with pentagonal links was found in 1954 by F. Liebau, the origin of which has been explained by Kh. S. Mamedov. In conclusion, the silicon-oxygen nets composed of wollastonite chains and xonotlite bands were described.

In his paper on the crystal chemistry of uranyl compounds, W. H. Zachariasen showed very convincingly, on the basis of valence bonds, the reality of the uranyl group for 6-coordinated uranium, even in such compounds as $Mg(UO_2)O_2$ and $Ca(UO_2)O_2$.

Depending on the size of the cation Mg^{2+}, Ca^{2+}, or Ba^{2+}, these compounds show variations in structure, but in all cases the $UO_2{}^{2+}$ group is present although in the "uranates" the conditions for its existence are less favorable than in the uranyl salts, in which the cation function of $UO_2{}^{2+}$ is very clear. Zachariasen used sodium uranyl acetate as an example.

At the opening meeting, J. D. Bernal gave a long and thorough report on the "Principles of the crystal chemistry of molecular crystals", and at the closing meeting of the 2nd crystal chemistry section he presented a paper on the modern theory of liquids.

J. Wyart and G. Sabatier (University of Paris, France), in a paper entitled "Formation of granite magma from pelitic sediments and the phases in equilibrium with it," reported that in an autoclave, at 2000 atm. granite begins to melt at 700°C.

Sabatier experimented with melting of sedimentary rocks composed of quartz, hydromica (illite) formed from kaolinite by adsorption of potassium chlorite, and a small amount of alkaline earth carbonates, and succeeded in fusing the rock at 800°C and pressure of 1200 atm. To check the attainment of equilibrium, the experiments were repeated under the same conditions with mixtures of chemically pure components. The crystalline substances obtained included biotite, cordierite and, in some experiments, hercynite--$FeAl_2O_4$.

The authors believe that in experiments of longer duration the metastabl products disappear and the melt approaches the composition of granitic magma. This process may explain the formation of granite magma as a result of tectonism (Lujeon's theory). The melt becomes a solvent for the surrounding rocks.

The interesting paper by I. G. Ismail-Zade (Baku, Azerbaidjan SSR) on the crystal structure of some ferroelectric substances dealt with the crysta chemistry of compounds with the perovskite structure--$CaTiO_3$. Many sub stances of more complex composition involving high valance elements have this structure, for example $Pb(Sc_{1/2}Nb_{1/2})O_3$ (with doubled dimension of th unit cell) or $Pb(Nb_{2/3}Ni_{1/3})O_3$, which forms a continuous isomorphous series with $Pb(Nb_{2/3}Mg_{1/4})O_3$ (with tripled dimension of the unit cell), and the compound $Pb(Fe_{2/3}W_{1/3})O_3$, which differs from the above compounds in having Fe^{3+} and W^{6+} ions in statistically random distribution.

The metaniobates of calcium, strontium, and barium are not iso-structur with the ferroelectric lead metaniobate and do not have ferroelectric properties. The properties of all synthesized crystals were studied above and below the Curie point.

K. Dornberger-Schiff, Hoehne and Kulpe (Berlin) reported on the structure of lautite (CuAsS). After a criticism of the previously obtained data on the structure of this mineral, they showed that the structure of lautite may be derived from diamond structure by allowing one-third of the atom positions to be occupied by copper, arsenic, and sulfur. Arsenic plays a double role in this structure. Each copper atom is surrounded by three atoms of sulfur and one of arsenic, each arsenic atom, by one copper and one sulfur atom, and each sulfur atom, by three copper atoms and one arsenic atom. This arrangement is that of the rhombic [orthorhombic] space lattice.

V. A. Frank-Kamenetskii (Leningrad) read a paper on isomorphism and mixed layer intergrowths in clay minerals. The mixed layer intergrowths explain the false impression of esceptionally extensive isomorphism among clay minerals.

G. Donnay and J. D. H. Donnay (Washington, U. S. A.) reported a new hypothesis of solid state transformations in feldspars.

C. H. MacGillavry and I. G. Palm (University of Amsterdam), in their paper on the structure of the urea sodium chloride hydrate and the effect of urea on the crystal habit of halite, described new investigations of this phenomenon.

At one of the general meetings, I. I. Shafranovskii (Leningrad) reported on the further development of Fedorov's crystallochemical analysis, i. e., of the determination of substances by the external form of their crystals. The problem of determination of substances by interfacial angles has been solved completely. However, the form of crystals is a function of crystal structure and of the medium from which they separate, and it is possible, therefore, to judge of the physicochemical state of the medium from the form of the crystals. The crystal habits of a given substance, if the conditions of their formation are known, may be used as indicators of the physicochemical character of the medium. The deviation of real crystals from the ideal provides information on the movement of currents feeding the growing crystals. For further refinement in such studies the growth markings on the crystal faces must also be taken into consideration.

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V. V. Shcherbina

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